Journal of Polymer Science: Part C, Polymer Symposia, No. 4

INTERNATIONAL SYMPOSIUM ON

Macromolecular Chemistry

Paris 1963

PART 1

Held under the auspices of the
International Union of Pure and Applied Chemistry
Paris, July 1-6, 1963

edited by *M. Magat*

Laboratoire de Chimie Physique de
la Faculte des Sciences de Paris, Paris, France

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JOURNAL OF POLYMER SCIENCE, PART C, *Polymer Symposia*

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Introduction

C'est au nom de mon collègue et ami Monsieur le Professeur Champetier, Membre de l'Institut, et en mon nom personnel que, tous les deux Présidents de cette manifestation, nous proclamons ouvert le Symposium International de Chimie Macromoléculaire qui va tenir ses assises à Paris pendant six jours.

Qu'il nous soit permis tout d'abord de remercier M. le Ministre d'Etat Chargé de la Recherche Scientifique d'avoir bien voulu accorder son haut patronage à notre réunion, et de saluer M. le Délégué Général à la Recherche Scientifique et Technique qui a tenu à montrer, par sa présence, tout l'intérêt qu'il porte et qu'il désire porter encore plus au développement de la Chimie Macromoléculaire jusque dans ses implications industrielles. Enfin que M. le Directeur Général du Service des Relations culturelles reçoive ici, dès l'abord, l'expression de notre gratitude pour le soutien si efficace qu'il a bien voulu accorder à notre Comité d'Organisation.

Cela dit, nous voudrions exprimer à tous les participants le plaisir qu'éprouvent les Présidents, le Comité d'Organisation et le Comité Scientifique à souhaiter la bienvenue la plus cordiale à tous les collègues et à tous les éminents savants qui si nombreux, ont répondu à notre appel, venant de tant de lointaines et diverses contrées du Monde. Nous éprouvons, à l'aspect de ces rencontres si favorables au développement pacifique des relations humaines un réconfort chaque fois renouvelé même si, comme aujourd'hui, nous devons regretter amèrement que les représentants de certains pays n'aient pas été, en dépit de nos efforts, autorisés à franchir nos frontières.

Nous éprouvons également une très grande tristesse à ne plus voir parmi nous deux éminents savants pour qui nous avions une très haute estime et une amicale affection.

Le Professeur Antonio Nasini, Directeur de l'Institut de Chimie de Turin, est décédé brusquement le 20 janvier 1963 à l'âge de 62 ans.

Le Professeur Alexander Vasilievich Topchiev, Vice Président de l'Académie des Sciences de l'Union des Républiques Socialistes Soviétiques, Directeur de l'Institut de Synthèse Pétrochimique de Moscou, a été emporté brutalement le 27 décembre 1962, à l'âge de 55 ans.

Qu'il nous soit permis—avant de commencer nos travaux—d'adresser à la mémoire des deux disparus un hommage ému, et à leurs familles, leurs amis, leurs collègues scientifiques, nos condoléances profondément attristées ainsi que l'expression de toute notre sympathie que nous manifesterons, si vous le voulez bien, en nous levant et en observant une minute de silence.

Mesdames, Messieurs, vous avez pu observer que le programme de ce Symposium était assez étroitement limité à deux types de préoccupations

différentes et peut-être me pardonnerez-vous si je tente—très brièvement rassurez-vous—d'en dégager les significations générales telles qu'elles sont apparues aux organisateurs de cette réunion.

(1) Les exposés formant un premier groupe de communications sont consacrés d'une part à l'étude des cinétiques de polymérisations effectuées dans des conditions spéciales, et d'autre part à l'étude des propriétés des copolymères à longues séquences. Sans doute ces sujets ont-ils retenu notre attention à cause de leur caractère de nouveauté et parce qu'ils sortent des chemins battus ce qui nous permettait d'ailleurs—pourquoi ne pas l'avouer?—de pas être submergés par un nombre excessif de communications sans doute toutes intéressantes mais qu'il aurait été difficile de contenir dans un programme raisonnablement limité. Mais aussi je dois souligner que les deux types de sujets, en dépit de leur diversité apparente, procèdent, tout au moins à mes yeux, de la même préoccupation profonde: celle de contrôler et de maîtriser la matière en établissant progressivement un ordre voulu, de plus en plus rigoureux, là où règnait auparavant le désordre et l'incertitude. Cela apparaît avec évidence avec le choix de l'étude des mécanismes de la polymérisation stéréospécifique; cela apparaît aussi pour la polymérisation en milieu ordonné qu'il s'agisse de la phase solide ou de la phase gel. Enfin cela est clair encore pour les copolymères séquencés ou greffés, dont les molécules—au lieu d'être composées de deux constituants répartis au hasard—sont véritablement conçues selon un plan voulu et possèdent des propriétés qui conduisent à la réalisation de nouvelles espèces de substances régulièrement structurées, qu'il s'agisse des gels mésomorphes ou des polymères organisés que ceux-ci permettent de fabriquer.

(2) Si le premier groupe de sujets correspond nettement au désir d'établir plus d'ordre et plus de régularité, le choix du deuxième groupe—avec les propriétés électroniques des polymères de synthèse et des polymères naturels—repose sur des préoccupations d'origines très différentes. Celles-ci sont en quelque sorte l'écho de l'évolution spectaculaire de la physicochimie dans ce domaine que l'on a appelé, de façon assez criticable d'ailleurs, la physique du solide.

Et encore faut-il là à nouveau souligner deux orientations de pensée différentes.

En ce qui concerne les hauts polymères de synthèse, il s'agira d'étudier des possibilités de transfert de charge ou d'énergie dans la masse d'un échantillon macroscopique avec toutes les implications que peuvent avoir les résultats trouvés, dans le domaine des applications électroniques par exemple. Cela impose la possibilité de ces transferts non seulement au sein de la macromolécule elle même, mais aussi et surtout entre les diverses macromolécules.

En ce qui concerne les hauts polymères naturels—c'est-à-dire essentiellement les acides nucléiques et les protéines—le même problème que ci-dessus se pose, mais il s'agit alors du problème du transfert au sein d'une macromolécule unique constituant un échantillon microscopique de

matière délicatement organisé et baignant dans une solution électrolyte. Là c'est la biologie fondamentale qui se trouve directement intéressée.

Cela dit, et pour en revenir au programme général de ce symposium, il pourrait apparaître qu'entre les deux groupes de sujets qui le constituent à savoir l'étude de la régularité et l'étude des propriétés quantiques, il n'existe aucune autre ressemblance que celle qui procède de la nouveauté, d'ailleurs toute relative, des questions posées.

Il est peut-être permis néanmoins de voir un peu plus loin. Je me contenterai seulement de souligner que les propriétés électroniques d'un fragment de haut polymère dépendent entre autres d'une part des régularités de structure de chacune des macromolécules qui le forment, et d'autre part des régularités de structure de leur ensemble. Si cela est bien vrai, alors on voit que s'estompe largement une différence qui pouvait paraître criante aux esprits sensibles et que l'étude du premier groupe de phénomènes semblera utile sinon indispensable, à l'étude du second groupe.

Ainsi donc, de ce point de vue, notre Symposium présente-t-il une certaine unité qui apparaîtra encore plus clairement lorsque, dans un avenir prochain, auront été réalisés les progrès que nous sommes auhourd'hui en droit de prévoir.

Mais ce n'est pas ici l'endroit de se livrer à d'imprudentes vues sur l'avenir et nous nous hâtons de revenir au présent en commençant nos travaux sans plus attendre. Je devrais donc maintenant céder la Présidence de la séance à M. le Professeur Natta. Malheureusement M. Natta, de même que M. Staudinger, n'ont pu à leur grand regret se rendre à notre invitation à cause d'ennuis de santé. Je suis sûr d'exprimer nos sentiments unanimes en leur adressant nos voeux très affectueux de prompt rétablissement. C'est donc le Professeur Melville, Directeur du D.S.I.R., qui voudra bien remplacer M. Natta dans sa charge.

Il nous reste, Mesdames et Messieurs, à vous souhaiter à tous bon courage et mérité succès.

Charles Sadron

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MECHANISM AND KINETICS OF STEREOSPECIFIC POLYMERIZATIONS IN INHOMOGENEOUS MEDIA

JOURNAL OF POLYMER SCIENCE: PART C NO. 4, PP. 3–9

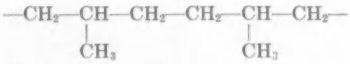
Principles of Conversional Polymerization of Unsaturated Hydrocarbons

B. A. KRENTSEL, L. G. SIDOROVA, and A. V. TOPCHIEV, *Institute of Petroleum Chemistry, Academy of Sciences of the U.S.S.R., Moscow, U.S.S.R.*

Stereospecific polymerization is regarded as a polymerization process resulting in the realization of one or several of the numerous possible configuration sequences of the monomeric links in the polymer chains. Therefore, stereospecific polymerization involves the selection of definite configurations of monomeric links, control of which leads to polymers with definite arrangements.

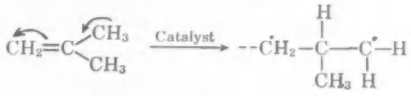
Besides the use of known principles of stereospecific polymerization, according to which complex metalloorganic catalysts (based on aluminum alkyls and titanium chlorides) are employed (these catalysts having become classical), searches have been made for new ways of initiating and controlling the growth of the polymeric chain to form stereoregular polymers. Of these new trends in stereospecific polymerization we should like to draw attention to polymerization involving transfer of the active center, known now as conversional polymerization.

Attention was first drawn to conversional polymerization by Topchiev and his co-workers[1] in a study of the polymerization of isobutylene with metalloorganic catalysts under conditions where the catalytic complex was a weak stereospecific catalyst. The resulting polymer had an anomalous structure



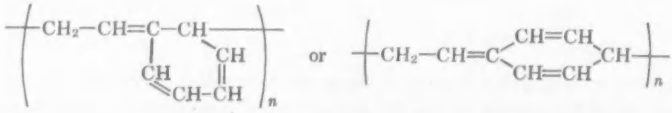
compared with those obtained earlier by polymerizing isobutylene with BF_3 or $AlCl_3$.[2] It may be assumed that during polymerization the active center was transferred owing to migration of a hydrogen atom.

During the formation of the π-complex from the π-electrons of the monomer and the free *d*-orbits of the transitional metal the electron density distribution in the monomer molecule is disturbed. If we suppose the double bond in the isobutylene molecule to be conjugated with the CH_3,[3] formation of the π-complex results in disturbance of the hyperconjugation, and for that reason the monomer molecule reacts in the 1,3-position.



An analogous mechanism can be put forth, for instance, for the conversional polymerization of propylene to polyethylene. With the higher α-olefins, $CH^2{=}CH{-}CH_2{-}R$, for which hyperconjugation is less probable,[3] conversional polymerization should proceed with difficulty.

During polymerization of the vinylaromatic hydrocarbon styrene, the active center should evidently be easy to transfer to the vinyl at the *ortho* and *para* position. This is analogous to addition (during a growth reaction) at the 1,4 and 1,6 positrons, which is very characteristic of the systems with conjugate bonds:



When the reaction takes such a course the benzene or quinoid structures are included in the fundamental chain of the polymer molecule. The possibility of this kind of addition in the polymerization of styrene was indicated also by Grassie and Kerr.[4]

The most suitable stereospecific catalysts for effecting the conversional polymerization of olefins to our opinion, are the comparatively weak ones[5–7] containing the components $TiBr_4$, TiI_4, $Ti(OR)_2Cl_2$, TiR_2Cl_2, or vanadium, chromium, or iron compounds in combination with aluminum alkyls, haloaluminum alkyls, complex sodium, lithium, aluminum, or boron alkylhydrides.

Recently we verified experimentally the occurrence of conversional polymerization in styrene polymerization with the catalytic system $Al(C_2H_5)_3 + VOCl_3$. A small quantity of a fraction differing in properties from atactic and isotactic polystyrene was isolated from the resulting polystyrene. Insoluble in conventional solvents, the product had a melting point of about 310–315°C. Infrared absorption spectra (Fig. 1 curve *a*) established the presence in this fraction of aromatic nuclei substituted in the *para* position, this being evidenced by an absorption band with a maximum at 809 cm.$^{-1}$ which is the characteristic band of 1,4-disubstituted benzene rings.[8]

As well as the *para*-substituted benzene nuclei the polymer also contains monosubstituted benzene nuclei, as is indicated by two characteristic absorption bands with maxima at 700 and 750 cm.$^{-1}$

From the above considerations the formation of such a product can be readily accounted for.

One more interesting feature of the structure of polystyrene obtained with the $Al(C_2H_5)_3 + VOCl_3$ catalyst should be pointed out.

In the infrared absorption spectra of the benzene-insoluble (at 20°C.) fractions of synthesized polystyrenes (Fig. 1 curve *b*), the intensities of the two characteristic bands of the monosubstituted benzene ring are, as a rule, unequal: the 700 cm.$^{-1}$ band is more intense than the other band of out-of-plane deformational vibration of the C—H aromatic ring with its maximum near 750 cm.$^{-1}$. The inequality of intensities as well as the very value of the

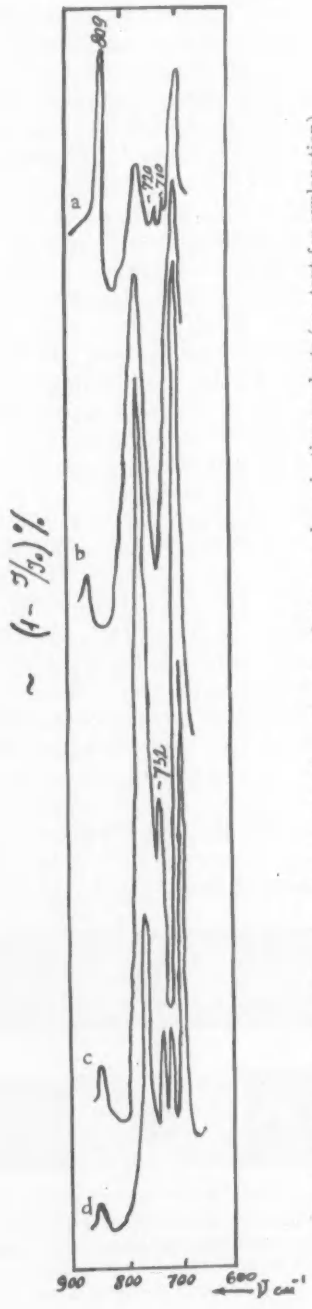


Fig. 1. Infrared absorption spectra in the 600–900 cm.$^{-1}$ range of styrene polymerization products (see text for explanation).

wave number (745–750 cm.$^{-1}$) at the maximum of the second band are an indication of the fact that the benzene rings of the synthesized polystyrenes are attached through —$(CH_2)_n$— bridges.[8,9]

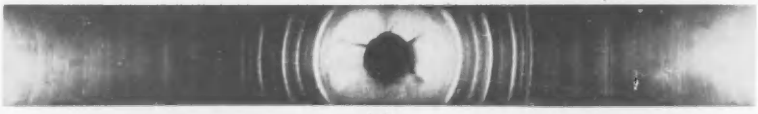
In a number of spectra of other polystyrene samples (Fig. 1 curve *c*) a band assigned to the methylene chain $(CH_2)_n$, where $n \geq 2$, with a peak at 732 cm.$^{-1}$ is observed in the explicit form.[10] At the same time the inequality of intensities of the 700 and 750 cm.$^{-1}$ bands increases.

This can be accounted for only by an increase in the percentage of polymeric cells with intermediate methylene links in the polystyrene samples.

Besides this, a double band at 710–720 cm.$^{-1}$ is observed between the 700 and 750 cm.$^{-1}$ bands in the infrared absorption spectra of a number of polymers (Fig. 1 curve *d*). This 710–720 cm.$^{-1}$ doublet is characteristic of the polymethylene chain and is indicative of a high degree of regularity of the polymethylene chains included in the polystyrene chain, as is observed for crystalline polyethylenes.[11] With the appearance of the polyethylene doublet, in a number of spectra the inequality of intensities of the 700 and 750 cm.$^{-1}$ bands of the monosubstituted benzene nucleus is observed to increase still further.

In this connection the assumption may be put forth that simultaneously with the growth of the "connecting" polymethylene bridges the relative amount of "elongated" links also increases. An approximate estimate of the relative intensities of the 700–750 and 710–720 cm.$^{-1}$ bands showed the share of polyethylene structure to amount to a few dozen per cent, but these fractions usually constituted an insignificant part of the total quantity of the product. An x-ray study of the polymers was also carried out. The polymer samples were studied by the method used for investigating powders in 57.29 mm. diameter PKY type chambers, radiation from an iron cathode at 30 kv. and an emission current of 12 ma. being used. The photographs were measured in the usual manner and the relative intensity of the reflection was determined visually by a five-point scale.

This x-ray investigation of the samples revealed that they show a large number of reflections, some of them being in the range of wide reflection



(*a*)

(*b*)

Fig. 2. X-ray photograph of (*a*) product obtained by polymerization of styrene with the catalytic system $Al(C_2H_5)_3 + VOCl_3$; (*b*) artificial 1:1 mixture of polystyrene and polyethylene (by weight).

angles (Fig. 2). The central region of the photograph is darkened insignificantly. The x-ray type resembles that of crystalline form of polyethylene in its reflections with interplanar distances d of 4.63, 3.78, 2.50, and 1.75 A.

The presence of a crystalline polystyrene structure can also be traced by the presence of reflections with $d = 4.12$ and 3.65 A. However, in most cases no crystalline polystyrene structure was detected; evidently, the polystyrene is in a roentgenomorphic state.

Polymethylene structure was detected in all cases where $Al(C_2H_5)_3$ was employed as a catalyst component. Apparently, the ethylene evolved during interaction between the catalyst components enters into copolymerization with the styrene However, the presence of long polymethylene chains with a benzene ring at one end and attached by their other end to the main chain of the polystyrene molecule supports the assumption that their formation occurred quite independently, after which they are "innoculated," as it were, onto the polystyrene molecules, disturbing their crystalline structure.

Conclusions

The possibility of conversional polymerization has been demonstrated by the example of styrene polymerization.

The probable mechanism of conversion polymerization was discussed.

In the polymerization of styrene with catalysts including $Al(C_2H_5)_3$ as one of the components a copolymer of ethylene with styrene has been separated from the reaction products.

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Synopsis

The possibility of conducting polymerization with the transfer of an active center within the monomer molecule a process which could be termed "conversion polymerization," is discussed. The polymerization of isobutylene on organometallic catalysts under conditions where the catalytic complex behaved like a weak stereospecific catalyst yielded a polymer having an abnormal structure in comparison with the structure obtained when

isobutylene was polymerized in the presence of BF_3 and $AlCl_3$. The transfer of an active center caused by the migration of a hydrogen atom appeared to occur during polymerization. A possible mechanism of such a phenomenon is suggested to involve a disturbance in the distribution of the electron density in the monomer during the formation of a π-complex from the π-electrons of the monomer and free *d*-orbital electron of the transition metal. If in the molecule of isobutylene the double bond is conjugated with $—CH_3$, the formation of a π-complex disturbs the hyperconjugation and the monomer molecule reacts at position 1,3. A similar mechanism can be suggested for the conversion polymerization of propylene to polyethylene. For the α-olefins of high molecular weight, for which the hyperconjugation is less probable the conversion polymerization will proceed with difficulty. During the polymerization of styrene the transfer of the active center in the positions *ortho* and *para* to the vinyl group would take place easier. This is similar to the addition (at the reaction of growth) to the 1,4 and 1,6 positions which is very characteristic of the systems with conjugated bonds. When the reaction takes this course, benzene or quinoid structures enter into the main chain of a polymeric molecule. This surmise was experimentally confirmed by a studying of the stereospecific polymerization of styrene. The most suitable catalysts for the conversion polymerization of olefins, are weak stereospecific catalysts with the following components: $TiBr_4$, TiI_4, $Ti(OR)_2Cl_2$, TiR_2Cl_2, or compounds of vanadium, chromium, or iron in conjunction with aluminum alkyls, halogen aluminum alkyls, complex sodium, lithium aluminum, boron alkylhydrides. In the presence of strong complex catalysts the addition must proceed at position 1,2 on account of the stronger interaction of π-electrons and catalysts.

Résumé

Une discussion des concepts modernes relatifs au mécanisme de la polymérisation stéréospécifique des alpha-oléfines, nous permet de suggérer la possibilité d'effectuer des polymérisations par transfert d'un centre actif à l'intérieur de la molécule de monomère. Un procédé de cette sorte peut être appelé 'polymérisation de conversion'. L'étude de la polymérisation de l'isobutène au moyen de catalyseurs organométalliques dans des conditions où le complexe catalytique se comporte comme un catalyseur faiblement stéréospécifique. Le polymère résultant possède une structure anormale comparée à la structure du polymère obtenu quand l'isobutène est polymérisé en présence de BF_3 et d'$AlCl_3$. Le transfert d'un centre actif dû à la migration d'un atome d'hydrogène semble se produire au cours de la polymérisation. Examinons le mécanisme possible d'un tel phénomène. Au cours de la formation d'un complexe π d'une molécule de monomère possédant un centre actif résultant de l'interaction des électrons π du monomère et des électrons libres de l'orbitale d du métal de transition, la répartition de la densité électronique dans la molécule de monomère est perturbée. Si dans la molécule d'isobutène la double liaison est conjuguée avec $C{=}CH_2$, la formation d'un complexe π perturbe l'hyperconjugaison et la molécule de monomère réagit en position 1,3. Un mécanisme semblable peut être proposé par exemple pour la polymérisation de conversion du propylène en polyéthylène. Chez les alpha-oléfines $CH_2{=}CH—CH_2—R$ à poids moléculaire élevé, pour lesquelles l'hyperconjugaison est moins probable la polymérisation de conversion s'effectuera difficilement. Lors de la polymérisation du styrène, le transfert du centre actif en position ortho et para par rapport au groupement vinylique s'effectuera sans aucun doute facilement. Ceci est semblable à l'addition (lors de la réaction de croissance) en position 1,4 et 1,6 particulièrement caractéristique des systèmes à liaisons conjuguées. Quand la réaction suit cette voie, des structures benzénique et quinonique se présentent dans la chaîne principale de la molécule polymérique. Cett supposition a été confirmée expérimentalement lors de l'étude de la polymérisation stéréospécifique du styrène. En ce qui concerne la polymérisation de conversion, suivant l'opinion des auteurs, les catalyseurs les plus souhaitables sont ceux qui sont faiblement stéréospécifiques avec les composants suivants: $TiBr_4$, TiI_4, $Ti(OR)_2Cl_2$, TiR_2Cl_2 ou

des composés du vanadium, du chrome, du fer en présence de dérivés alcoyles aluminium, de complexe de sodium, de lithium aluminium, d'hydrure d'alcoyle bore. En présence de catalyseurs fortement complexés l'addition s'effectuera en position 1,2 à cause de l'interaction plus énergique entre les électrons π et les catalyseurs.

Zusammenfassung

Die Möglichkeit, eine Polymerisation mit Übertragung eines aktiven Zentrums innerhalb der Monomermolekel durchzuführen, wird diskutiert. Ein solcher Prozess kann als "Umlagerungspolymerisation" bezeichnet werden. Die Polymerisation von Isobutylen an organometallischen Katalysatoren unter Bedingungen eines schwach stereospezifischen Verhaltens des katalytischen Komplexes lieferte ein Polymeres mit einer im Vergleich zu der bei der Polymerisation von Isobutylen in Gegenwart von BF_3 und $AlCl_3$ erhaltenen Struktur, abnormalen Struktur. Während der Polymerisation scheint eine durch Wanderung eines Wasserstoffatoms bedingte Übertragung eines aktiven Zentrums aufzutreten. Als möglicher Mechanismus einer solchen Erscheinung wird eine Störung der Elektronendichteverteilung im Monomeren während der Bildung eines π-Komplexes aus den Elektronen des Monomeren und dem freien *d*-Orbital des Übergangsmetalles angenommen. Wenn in der Isobutylenmolekel die Doppelbindung mit CH_3 konjugiert ist, wird die Hyperkonjugation durch die Bildung eines π-Komplexes gestört und die Monomermolekel reagiert in der 1,3-Stellung. Ein ähnlicher Mechanismus wird für die Umlagerungspolymerisation von Propylen zu Polyäthylen vorgeschlagen. Bei α-Olefinen mit höherem Molekulargewicht, bei welchen Hyperkonjugation weniger wahrscheinlich ist, wird die Umlagerungspolymerisation nur schwierig eintreten. Bei der Polymerisation von Sytrol könnte die Übertragung des aktiven Zentrums in *ortho*- und *para*-Stellung zur Vinylgruppe leichter stattfinden. Das ist der Addition (bei der Wachstumsreaktion) in 1,4- und 1,6-Stellung ähnlich, die für Systeme mit konjugierten Bindungen so charakteristsich ist. Bei Auftreten einer solchen Reaktion enthält die Hauptkette einer Polymermolekel benzoide oder chinoide Strukturen. Das konnte durch eine Untersuchung der stereospecifischen Polymerisation von Styrol bestätigt werden. Die besten Katalysatoren für die Umlagerungspolymerisation von Olefinen sind schwach stereospezifische Katalysatoren mit folgenden Komponenten: $TiBr_4$, TiI_4, $Ti(OR)_2Cl_2$, TiR_2Cl_2 oder Vanadin-, Chrom- und Eisenverbindungen gemeinsam mit Aluminiumalkylen, Halogenaluminiumalkylen, komplexen Natrium-, Lithium-, Aluminium- und Boralkylhydriden. In Gegenwart starker Komplexkatalysatoren muss die Addition wegen der stärkeren Wechselwirkung zwischen π-Elektronen und Katalysatoren in 1,2-Stellung erfolgen.

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Reactions Elémentaires de la Polymérisation du Propylène à la Surface du $TiCl_3$

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Considérée du point de vue due caractère de la réaction, la polymérisation du propylène sur $TiCl_3$ est une réaction en chaîne.

Les réactions en chaîne des polymérisations ioniques, où—en contraste avec les réactions en chaîne radicalaires—on ne peut pas supposer une terminaison mutuelle des centres croissants, peuvant être expliquées par l'hypothèse d'un état stationaire dans lequel une partie des centres actifs assurerait la croissance et l'autre partie serait présente sous une forme moins active.

Une formule a été proposée[1] pour traiter la polymérisation en chaîne par les ions libres:

$$-\frac{d[M]}{dt} = \frac{k_p K^{1/2}[Cat]_0^{1/2}[M]}{1 + \frac{k_{tr}[HX]}{k_i[M]}} \quad (1)$$

où k_p, k_{tr}, k_i sont les constantes de croissance, de transfert et de réamorçage, K est le constante de dissociation, [HX] est la concentration de l'agent de transfert, et $[Cat]_0$ est la concentration initiale du catalyseur. La concentration totale des centres actifs est ainsi divisée en une partie des centres "vifs" $[M^{\ominus}]$ et l'autre partie des centres "dormants" $[X^{\ominus}]$ qui ont été formés par le transfert de chaîne et dont la réactivité est réduite.

Nous allons maintenant noter les caractéristiques fondamentales de la polymérisation du propylène sur $TiCl_3$.

(*1*) La masse moléculaire ne dépend pratiquement pas du degré de conversion (Fig. 1)—un témoignage de ce que la réaction est une réaction en chaîne.

(*2*) La masse moléculaire ne dépend pratiquement pas de la concentration du monomère (Fig. 2) et ne dépend que très peu de la concentration du triéthylaluminium (Fig. 3); ceci signifie que le transfert avec le monomère est la réaction essentielle déterminant la masse moléculaire.

(*3*) La vitesse de réaction en fonction de la concentration du triéthylaluminium aussi bien qu'en fonction de la concentration du monomère passe par un maximum;[1,2] ceci prouve que le monomère sorbé réagit au cours de la réaction avec le triéthylaluminium sorbé.

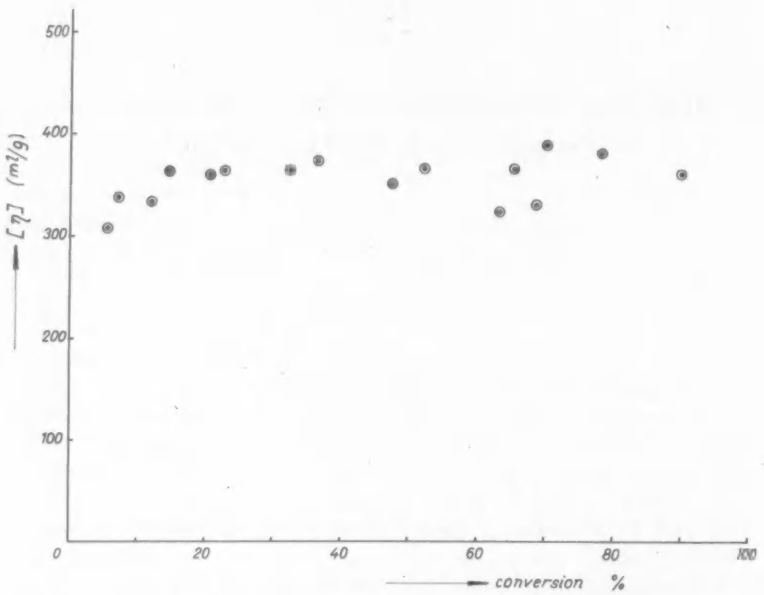


Fig. 1. Variation de la masse moléculaire en fonction du taux de conversion: t = 50°C, $[C_3H_6]$ = 2,3 mole/l, $[TiCl_3]$ = 0,77 g/l, surface spécifique: 7 m²/g, $[AlEt_3]$ = $3{,}4.10^{-2}$ mole/l.

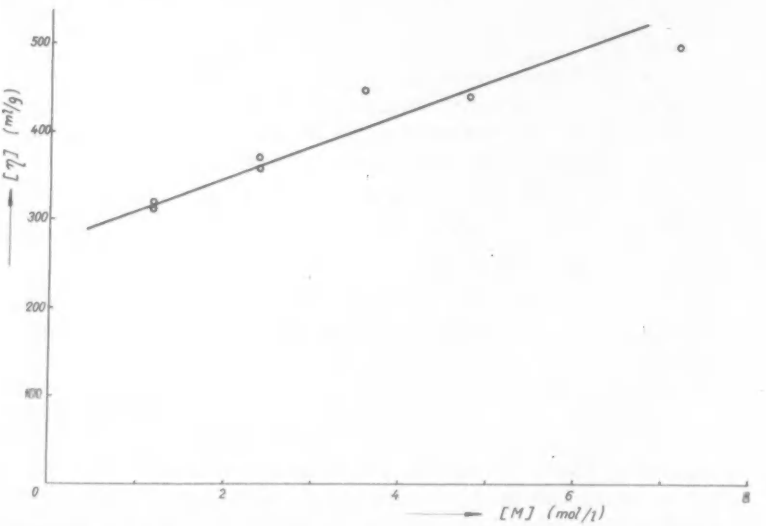


Fig. 2. Variation de la masse moléculaire en fonction de la concentration du monomère: t = 50°C, $[TiCl_3]$ = 0,77 g/l, $[AlEt_3]$ = $3{,}4.10^{-2}$ mole/l.

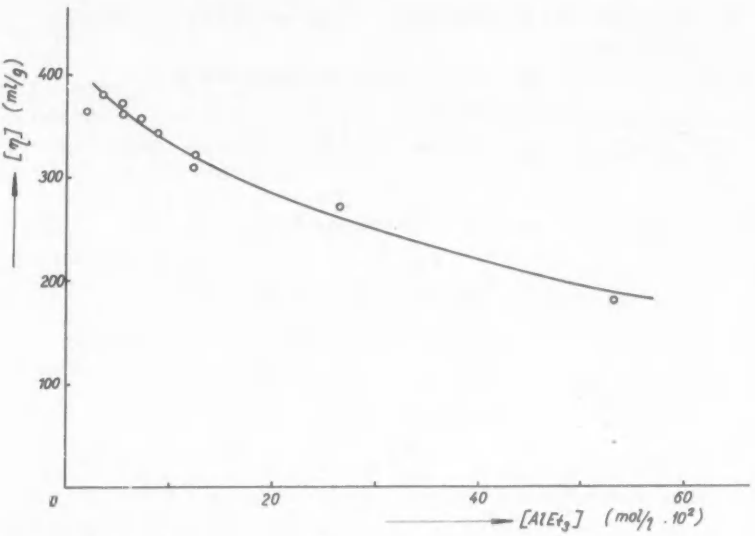


Fig. 3. Variation de la masse moléculaire en fonction de la concentration du triéthylaluminium: t = 50°C, [$TiCl_3$] = 0,77 g/l, [C_3H_6] = 2,3 mole/l.

(*4*) La vitesse de réaction est proportionelle à la surface du $TiCl_3$ (Tableau I).

TABLEAU I

Variation de la Vitesse de Polymérisation en Fonction de la Surface tu $TiCl_3$

Quantité du $TiCl_3$, g/l	Surface du $TiCl_3$, m^2/g	Constante de la vitesse de réaction × 10^3, min^{-1}	Vitesse spécifique de réaction × 10^4, l./min., m^2
0,85	7	8,0	1,34
0,25	25	7,9	1,26
0,07	90	8,5	1,35

(*5*) L'addition de l'hydrogène cause une réduction de la masse moléculaire, qui est aussi accompagnée par une réduction de la vitesse de réaction.[5]

(*6*) Certaines substances ayant un caractère donneur d'electrons agissent en tant que retardateurs spécifiques.[3]

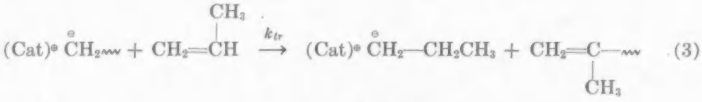
Nous allons formuler maintenant les réactions élémentaires qui constituent la réaction en chaîne de la polymérisation. Ic: $(Cat)^{\oplus}$ représente le cation complexe $(TiCl_3 \cdot AlR_2)^{\oplus}$

a. Croissance

$$(Cat)^{\oplus}\overset{\ominus}{C}H_2\sim + CH_2{=}\underset{\displaystyle CH_3}{\underset{|}{CH}} \xrightarrow{k_p} (Cat)^{\oplus}\overset{\ominus}{C}H_2\sim\sim \qquad (2)$$

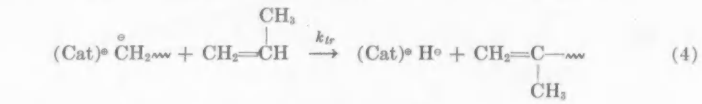
b. Transfert avec le Monomère. Nous prenons en consideration les réactions suivantes.

(1) Rupture de la chaîne avec transfert de l'anion hydrure:[4]



(3)

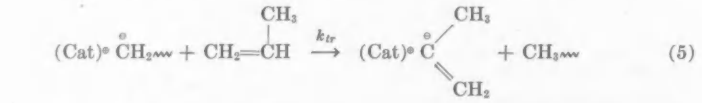
(2) Transfert de l'anion hydrure[4] du monomère au centre actif:



(4)

Le même centre est formé aussi lors du transfert avec l'hydrogène.

(3) Transfert d'un proton au centre actif:

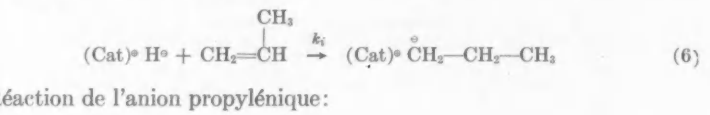


(5)

Tandis que la réaction (3) donne naissance aux centres actifs tous identiques, les réactions (4) et (5) donnent naissance aux centres actifs d'une réactivité réduite. Comme la réaction (5) est suivie par l'addition d'un monomère, un groupe terminal à liaison double est formé aussi dans ce cas.

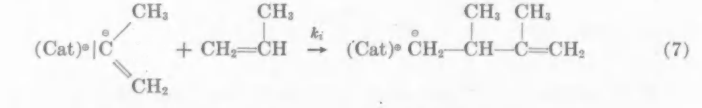
c. Réamorçage. Dans le cas du transfert suivant l'équation (3), le réamorçage est identique avec la réaction de la croissance, c'est porquoi nous allons examiner seulement deux réactions de réamorçage.

(1) Réaction de l'anion hydrure:



(6)

(2) Réaction de l'anion propylénique:



(7)

La vitesse de la réaction de croissance sera donnée par:

$$V_{\text{totale}} = -d[\text{M}]/dt = k_p\theta_{\text{C}_1}\theta_{\text{M}}[\text{S}] \tag{8}$$

où θ_{C_1} est la fraction de la surface du $TiCl_3$ occupée par les centres "vivants" $(Cat)^{\oplus\ominus}CH_2$, θ_M est la fraction de la surface du $TiCl_3$ occupée parl le monomère, et [S] est la surface totale active du $TiCl_3$.

Supposons, comme pour la polymérisation ionique en milieu homogène,[1] qu'a côté des centres "vivants" $C_1^{\ominus}$ il y a aussi des centres "dormants" $C_2^{\ominus}$ qui peuvent former les paires ioniques sorbés au sens des réactions men-

tionnés au-dessus: $(Cat^{\oplus})\ H^{\ominus}$ ou $(Cat^{\oplus})\ CH_2 = C^{\ominus}—CH_3$. A l'état stationaire il y aura

$$d\theta_{C_2}/dt = k_{tr}\theta_{C_1}\theta_M - k_t\theta_{C_2}\theta_M = 0 \tag{9}$$

La fraction de la surface occupée par le triéthylaluminium, qui est donnée par une constante d'adsorption[1,2,6] K_A, comprend alors les centres "vivants" aussi bien que "dormants," donc,

$$\theta_A = \theta_{C_1} + \theta_{C_2} \tag{10}$$

Les équations (9) et (10) donnent

$$\theta_{C_1} = [k_t/(k_{tr} + k_t)]\theta_A \tag{11}$$

Après substitution dans l'équation (8) on obtient l'expression pour la vitesse totale de la réaction

$$V_{\text{totale}} = \frac{k_t k_p}{(k_{tr} + k_t)} \cdot \frac{[S]K_M(M)K_A[A]}{(1 + K_M[M] + K_A[A])^2} \tag{12}$$

où K_M, K_A sont les constantes d'adsorption du monomère et du triéthylaluminium, et [A] est la concentration du triéthylaluminium.

Il a déjà été montré[1,2,7] que cette équation se conforme bien aux données expérimentales.

Le degré de polymérisation, si on néglige le transfert avec le triéthylaluminium, sera donné par

$$P_n \doteq k_p/k_{tr} \tag{13}$$

Comme on l'a déjà indiqué,[1] il faut distinguer dans la réaction de croissance sur les paires ioniques, deux réactions élémentaires consécutives. Dans le cas de la polymérisation sur une surface hétérogène le schéma comprend encore l'adsorption préalable des constituants.

Examinons maintenant les réactions élémentaires.

a. Adsorption du Propylène sur la Surface du $TiCl_3$ et sa Mobilité. La valeur de la constante de l'adsorption[1] $K_M = 0{,}16$ aussi bien que les isothermes d'adsorption (Table au II) montrent que le propylène n'est que faiblement adsorbé à la surface du $TiCl_3$ et partant de là la migration

TABLEAU II

Énergies de Sorption Libres Rélatives, Chaleurs de Sorption et Entropies de Sorption à la Surface du $TiCl_3$

Substance sorbée	ΔG, kcal/mole	ΔH, kcal/mole	ΔS, cal/mole °K
Propylène	+1,2		
n-Hexane	0		
Triéthylaluminium	−2,0	−35,1	−102
Acetylène	−4,3		
Propadiène	−6,0		

monomère adsorbé à la surface du $TiCl_3$ doit êntre facile et ne doit pas être l'élément déterminant la vitesse de réaction.

b. Adsorption du Triéthylaluminium. La constante d'adsorption K_A aussi bien que la détermination de la chaleur d'adsorption (Tableau II) montrent que le triéthylaluminium est adsorbé à la surface du $AlCl_3$ considérablement plus fort que le propylène.

Bien que le triéthylaluminium dissous soit partiellement dimerisé[8] aux températures de la polymérisation, les données cinétiques expérimentales[7] montrent que la dissociation est sans doute très rapide et que le triéthylaluminium entre dans l'expression pour la vitesse totale de réaction comme première puissance et non pas comme racine carrée selon Saltman.[6,9] De la chaleur d'adsorption on peut estimer que l'énergie d'activation de la migration du triéthylaluminium adsorbé à la surface du $TiCl_3$ s'éléve à au moins 15 kcal/mole.

Détermination des Energies d'Activation des Réactions Elémentaires

Partant de l'équation (12), l'énergie d'activation sera donnée par

$$E_{\text{totale}} = E_i + E_p - E_{tr} \tag{14}$$

Les valeurs de E_{totale}, $E_p - E_{tr}$, aussi bien que E_i sont indiquées dans le Tableau III.

TABLEAU III
Énergies d'Activation des Réactions Élémentaires

E_{totale} kcal/mole[a]	$E_p - E_{tr}$, kcal/mole	E_i, kcal/mole
10,8	−2,0	12,8

[a] Déterminé pour $TiCl_3$ avec la surface spécifique de 7 m^2/g.

Nous en tirons la conclusion que c'est le réamorçage qui détermine pratiquement l'énergie totale de l'activation. Il est probable que le réamorçage est accompagné par une migration de l'anion conjugé sorbé plutôt que par la migration du triéthylaluminium sorbé. La valeur de l'entropie d'adsorption[10] pour la sorption du triéthylaluminium est assez grande et il est probable que sa migration exigerait une énergie d'activation plus haute que celle correspondant à la valeur de E_i trouvée.

Partie Experimentale

Les réactits employés etaient *n*-hexane, rectifié, séché sur sodium et à nouveau rectifié en atmosphère d'azote; propylène, produit de Bunnawerke RDA, purifié par KOH, séché sur tamis moléculaire A5 et rectifié; triéthylaluminium, préparé par la méthode de Grosse et Mavity,[11] rectifié sous vide, exempt de Cl; α-$TiCl_3$, préparé par réduction du $TiCl_4$ avec l'hydrogène. La surface specifique de l'α-$TiCl_3$ de 7–9 m^2/g était déterminée par une méthode de sorption thérmique modifiée par Grubner.[12]

La vitesse de polymérisation était mèsurée par voie dilatométrique déjà décrite.[13]

Le degré de polymérisation moyen en nombre a été mesuré à partir des données viscosimétriques en employant les constantes de Danusso et Moraglio.[14] On a travaillé à la température de 140°C dans la tétraline. On a employé le viscosimètre[15] adopté pour le travail dans l'atmosphère inerte.

Les isothermes d'adsorption de *n*-heptane et propylène ont été déterminées par une méthode chromatographique.[16]

La chaleur de l'adsorption du triéthylaluminium a été mésurée directement en ajoutant une solution de triéthylaluminium à une suspension de $TiCl_3$ dans le *n*-heptane se trouvant dans le calorimètre. La masse de triéthylaluminium adsorbée a été déterminée partant de la concentration de triéthylaluminium en solution.

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Résumé

La polymérisation catalytique procédante par participation des paires ioniques en milieu homogène est comparée avec celle procédante à la surface hétérogène. En milieu homogène, la polymérisation atteint le caractère d'une réaction de chaine par le fait qu'à coté des centres "vivants" il y a aussi des centres "dormants" d'une activité reduite. En milieu hétérogène aussi on suppose l'existence de deux types de centres; les centres "dormants" sont formés par le transfert avec le monomère. Bien que ces deux cas se ressemblent, dans le cas du milieu hétérogène il faut prendre en considération aussi une chimisorption préalable de l'organo-métal et du monomère. Une expression a été déduite pour la vitesse de réaction totale d'où il ressort que la réinitiation, c'est-à-dire la réaction des centres "dormants" avec le monomère adsorbé est le phénomène le plus lent, étant caractérisé d'une énergie d'activation E_i = 12.8 kcal/mole.

La détermination de la chaleur d'absorption du triéthylaluminium aussi bien qu'une détermination approximative des chaleurs d'adsorption du propylène, de l'hexane et de l'acétylène montrent que le triéthylaluminium est adsorbé à la surface tu $TiCl_3$ très fort et que la réinitiation est probablement accompagnée par une migration, le long de la surface du $TiCl_3$, de l'anion conjugé formé par le transfert avec le monomère.

Synopsis

The catalytic polymerization with ion pairs in homogeneous medium has been compared to that proceeding at a heterogeneous surface. In homogeneous medium, the polymerization behaves as a chain reaction on account of the presence of "living" centers besides "dormient" centers (less reactive). In heterogeneous medium also one assumes the existence of two types of centers; the dormient centers are formed by transfer with monomers. Although both cases are similar, nevertheless in heterogeneous medium one should take into account the preliminary chemisorption of the organometal and of the monomer. An equation for the overall rate has been derived, which shows that the reaction of the monomers with "dormient" centers is the slowest step, being characterized by an activation energy E_i = 12.8 kcal/mole. The determination of the heat of absorption of triethylaluminium, as well as an evaluation of those of propylene, hexane and acetylene show that the triethylaluminium is very strongly absorbed on the surface of $TiCl_3$ and that the reinitiation is probably accompanied with the migration along the surface of $TiCl_3$ of the conjugated anion formed by transfer with monomer.

Zusammenfassung

Die unter Teilnahme von Ionenpaaren im homogenen Milieu verlaufender katalytische Polymerisation wird mit der heterogen an Grenzflächen verlaufender verglichen. Im homogenen Milieu erreicht die Polymerisation dadurch den Charakter einer Kettenreaktion, dass neben den "lebenden" Zentren auch "schlafende," mit einer herabgesetzten Aktivität vorhanden sind. Auch im heterogenen Milieu wird die Existenz von zwei Typen von Zentren angenommen; die "schlafenden" Zentren werden durch Übertragung mit dem Monomeren gebildet. Obgleich beide Fälle ähnlich sind, muss man im Falle des heterogenen Milieus doch auch eine vorangehende Chemisorption der metallorganischen Verbindung und des Monomeren in Betracht ziehen. Ein Ausdruck für die Bruttogeschwindigkeit der Reaktion wurde abgeleitet, aus welchem sich der Sekundärstart, d.h. die Reaktion der "schlafenden" Zentren mit dem adsorbierten Monomeren als der langsamste Vorgang mit einer Aktivierungsenergie E_i = 12,8 kcal/Mol ergibt. Die Bestimmung der Adsorptionswärme von Triäthylaluminium, sowie eine angenäherte Bestimmung der Adsorptionswärme von Propylen, Hexan und Acetylen zeigen, dass Triäthylaluminium an der Oberfläche von $TiCl_3$ sehr stark adsorbiert wird und dass der Sekundärstart wahrscheinlich von einer Wanderung des durch Übertragung mit dem Monomeren gebildeten konjugierten Anions entlang der Oberfläche von $TiCl_3$ begleitet wird.

Discussion

J. Pasquon (*Milan, Italie*): (*1*) Dans vos calculs vous supposez que l'état de la surface du $TiCl_3$ ne change pas avec le rapport Al/Ti. Avez-vous quelques données expérimentales en accord avec cette hypothèse? (*2*) Nous avons observé que lorsque la pression de propylène est $<$400–500 mm Hg (à 70°C), la vitesse globale de polymérisation diminue plus que proportionnellement à la pression du monomère. Ces résultats semblent en accord avec vos conclusions. Avez-vous des données expérimentales de ce type? (*3*) *Question posée par écrit.* Pour déduire vos équations cinétiques vous supposez que les "centres actifs" présents sur la surface du $TiCl_3$ se comportent de la même façon par rapport à l'adsorption du monomère et par rapport à celle de l'aluminium alcoyle. Avez-vous des données expérimentales qui peuvent confirmer cette hypothèse?

K. Veselý (*Institut de Chimie Macromoléculaire, Brno, Tchécoslovaquie*). (*1*) La vitesse de polymérisation initiale est toujours proportionnelle à la surface du $TiCl_3$ et dans le système pur il n'y a pas de période d'induction. Jusqu'à maintenant nous n'avons pas pu prouver cette hypothèse directement. (*2*) Nous n'avons pas de données expérimentales dans les domaines des petites pressions. (*3a*) La surface relative occupée par l'aluminium alcoyle (c'est-à-dire le nombres de centres actifs) est beaucoup plus grande que le nombre de macromolécules formées. Cela veut dire qu'une petite partie seulement des complexes Ti-Al présents réagit. (*3b*) La constante k_A trouvée par l'analyse cinétique est en accord avec les résultats obtenus par l'analyse de l'isotherme d'adsorption de $AlEt_3$ sur $TiCl_3$. (*3c*) Avec un grand excès de $AlEt_3$, on observe des périodes d'induction. (*3d*) La vitesse de polymérisation atteint un maximum en fonction de $AlEt_3$ et du monomère. Ces effets ont été trouvés seulement dans le domaine de hautes concentration en monomère.

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Optically Active Vinyl Polymers. VIII. Some Aspects of the Stereospecific Polymerization of Racemic α-Olefins

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INTRODUCTION

Despite the large number of papers published on the mechanism of stereospecific polymerization the detailed structure and reactivity of the active centers of the stereospecific catalysts is still rather obscure.

Some surprising aspects of the stereoselectivity of the catalyst prepared from $TiCl_3$ and AlR_3 have been recently noted in the investigation of the polymerization of the racemic 3-methyl-1-pentene and 4-methyl-1-hexene. As we have previously reported,[1] the polymer obtained from racemic 3-methyl-1-pentene or 4-methyl-1-hexene by $TiCl_3/Al(i-C_4H_9)_3$ catalysts can be separated by chromatographic methods in fractions having optical activity of different sign. Fractions having optical purity of 30% and more have been isolated: therefore at least some of the macromolecules are formed by different amounts of (*R*) and (*S*) monomers, the ratio between the enantiomeric monomers in a single macromolecule being 2 or even more.

Practically amorphous (atactic) fractions, partially crystallizable stereoblock fractions, and highly stereoregular isotactic fractions were resolved by the same method.

In principle two hypotheses* are suggested by these results: (*1*) the choice of one of the monomeric enantiomers is regulated by the first asymmetric group of the chain, that is, the alkyl group of the initiator or the first monomeric unit; (*2*) the remarkably different rate of polymerization of two antipods on the same catalytic center is due to the intrinsic asymmetry of the center arising either (*a*) from the arrangement of the atoms of the center of the catalyst surface or (*b*) from an asymmetric organic group included in the active center.

In order to evaluate the soundness of the first hypothesis, we have investigated the polymerization of racemic 4-methyl-1-hexene by catalysts

* The hypothesis of the existence of macromolecules having an odd number of very long stereoblocks should be discarded in view of the fact that also low molecular weight amorphous polymers, probably built up by a large number of very small stereoblocks. have been resolved.[1]

TABLE I Optical Rotatory Power in Hydrocarbon Solution of Fractions of Polypropylene Samples Obtained with Optically Active Stereospecific Catalysts in the Absence of Solvents

Fraction	Run A[a]			Run B[b]			
	%	α_D^{30} (l = 2 dm.)	$[\alpha]_D^{30}$	%	α_D^{30} (l = 1 dm.)	$[\alpha]_D^{30}$	$\bar{M}_\eta$[c]
Acetone-soluble	14.4	+0.025°	+3.9°	2.9	+0.050°	+0.9°	[d]
Acetone-insoluble, ethyl acetate-soluble	11.4	+0.010°	+1.9°	5.6	+0.040°	+0.4°	10,000
Ethyl acetate-insoluble, diethyl ether-soluble				17.4	+0.025°	+0.2°	120,000
Diethyl ether-insoluble, isooctane-soluble	21.6	—	—	14.4	—	—	180,000
Isooctane insoluble	52.6	—	—	59.7	—	—	270,000

[a] Catalyst: $(C_2H_5)_2OAl(i\text{-}C_5H_{11})_3/TiCl_3$, molar ratio = 5.0. Polymerization carried out at 80°C. and at atmospheric pressure. $\bar{M}_\eta$ of the fractions have not been determined.

[b] Catalyst: $(C_2H_5)_2OAl(i\text{-}C_5H_{11})_3/TiCl_4$, molar ratio = 10.0. Polymerization carried out at 60°C. and at 10 atm.

[c] Calculated following the equation:[18] $[\eta] = 1.93 \times 10^{-4} \bar{M}_\eta^{0.74}$.

[d] Molecular weight determined by cryoscopy in benzene: 750 ± 1000.

TABLE II. Properties of Polystyrene Obtained with the Use of Optically Active Catalysts

Catalyst	Temp., °C.	%[e]	α_D^{30}	$[\alpha]_D^{30}$	$\bar{M}_\eta$[a]	Solubility[b]
(*R*)-2-methylbutyllithium	−78	100	+0.030[c]	+0.2°	—	Acetone-soluble
(*R*)-2-methylbutyllithium/CrA_3	−78	95.6	+0.105°[d]	+0.6°	8.500	Acetone-soluble
	20–25	4.4	+0.015°[d]	+0.1°	50.000	Acetone-insoluble, benzene soluble

[a] Determined from viscometric data by use of the equation of Ang.[19]

[b] At the solvent boiling point.

[c] l = 1 dm.

[d] l = 2 dm.

[e] Based on the polymer total weight.

prepared from optically active organometallic compounds, and we have compared the optical activity of the polymers thus obtained with the optical activity of some fractions of polypropylene and polystyrene prepared by the same type of catalysts.

RESULTS

Polymerization of Propylene by Catalysts Obtained from Optically Active Organometallic Compounds

On polymerization of propylene by catalysts obtained from $TiCl_3$ or $TiCl_4$ and (+) tris-[(*S*)-2-methylbutyl]aluminum diethyl etherate having high optical purity (91%), not only the low molecular weight fractions but also the fractions having $\bar{M}_v$ as high as 120,000 are optically active, as shown in Table I.

The polymerization experiments were carried out with the use of the organometallic compound as solvent in order to have a low monomer/organometallic compound ratio and to favor the chain transfer processes with the organometallic compound with respect to the chain transfer with the monomer.[2]

The optical activity of the corresponding fractions obtained at atmospheric pressure by $TiCl_3$ catalyst, are higher than those obtained by $TiCl_4$ catalyst at 10 atm.; this result can be attributed both to the higher chain transfer with the monomer at 10 atm. and to the different catalyst used.

Starting with (+) tris-[(*S*)-2-methylbutyl]aluminum diethyl etherate as initiator the sign of the optical activity is positive and the optical activity decreases very rapidly by increasing $\bar{M}_v$ of the fraction.

The same results were obtained on polymerization of styrene with different catalytic systems. In this case also the optical activity is not markedly dependent on the stereoregularity of the polymer and rapidly decreases with increasing $\bar{M}_v$ of the sample (Table II).

Polymerization of (*R*)(*S*)-4-Methyl-1-hexene by Catalysts Obtained from Optically Active Organometallic Initiators

As reported in Table III, on polymerization of racemic 4-methyl-1-hexene by catalysts obtained from (+)-tris-[(*S*)-2-methylbutyl]-aluminum diethyl etherate and $TiCl_3$ or $TiCl_4$ the low molecular weight fractions are optically active, the values of the rotation being, in some cases, remarkably higher than those obtained in the corresponding experiments carried out with propylene or styrene.

Also in the case of racemic 4-methyl-1-hexene the optical activity of the polymer does not seem to be dependent on the stereoregularity of the fractions, the main factors influencing the optical activity being the ratio between the monomer and the aluminum alkyl compound and the molecular weight of the polymer.

TABLE III

Optical Activity in Benzene Solution of Fractions of Poly-4-methyl-1-hexene Obtained by Bulk Polymerization of the Racemic Monomer using (+)-Tris-[(*S*)-2-methylbutyl]aluminum Diethyl Etherate as Optically Active Catalyst Component

Fraction	Run A[a]				Run B[b]				Run C[c]			
	%	α_D (l = 1 dm.)[d]	$[\alpha]_D$[d]	$[\eta]$, dl./g.[e]	%	α_D (l = 1 dm.)[d]	$[\alpha]_D$[d]	$[\eta]$, dl./g.[e]	%	α_D (l = 1 dm.)[d]	$[\alpha]_D$[d]	$[\eta]$, dl./g.[e]
Acetone-soluble	5.7	+0.190°	+3.7°	[f]	5.6	+0.090°	×5.0°	[g]	4.8	+0.095°	+7.1°	—
Acetone-insoluble, ethyl acetate-soluble	6.9	+0.030°	+0.4°	0.16	11.3	+0.035°	+1.1°	0.12	8.2	+0.025°	+1.1°	0.15
Ethyl acetate-insoluble, diethyl ether-soluble	17.0	+0.025°	+0.3°	0.84	18.5	+0.040°	+1.1°	1.22	9.5	+0.015°	+0.8°	0.70
Diethyl ether-insoluble, diisopropyl ether-soluble	22.4	~0	~0	1.40	16.0	~0	~0	1.80	22.7	~0	~0	2.05
Diisopropyl ether-insoluble, isooctane-soluble	48.0	~0	~0	1.98	48.3	—	—	n.d.	54.8	~0	~0	5.45

[a] Catalyst: $(C_2H_5)_2OAl(i\text{-}C_5H_{11})_2/TiCl_3$; 9.3 moles olefin/mole AlR_3.

[b] Catalyst: $(C_2H_5)_2OAl(i\text{-}C_5H_{11})_2/TiCl_3$; 4.6 moles olefin/mole AlR_3.

[c] Catalyst: $(C_2H_5)_2OAl(i\text{-}C_5H_{11})_2/TiCl_4$; 1.4 moles olefin/mole AlR_3.

[d] At 20°C. for the acetone-soluble and acetone-insoluble, ethyl acetate-soluble fractions; at 50°C. for the other fractions.

[e] Determined at 120°C. in tetralin.

[f] Molecular weight determined by cryoscopy in benzene: 780 ± 50.

[g] Molecular weight determined by cryoscopy in benzene: 1000 ± 300.

TABLE IV

Polymerization of (*R*)(*S*)-4-Methyl-1-hexene in the Presence of Tris-[(*S*)-2-methylbutyl]-aluminum Diethyl Etherate and $TiCl_3$

	Polymerization conditions				Initial	Unpolymerized monomer		Polymer	
Run	AlR_3, moles/ mole $TiCl_3$	Olefin, moles/ mole AlR_3	Temp., °C.	Duration, hr.	monomer, g.	Weight, g.	α_D^{20}[a]	Weight, g.	$\Sigma_i\{[\alpha]_D\}_i w_i$[b]
A	4.0	9.3	25	1998	15.00	3.30	~0[c]	10.6	+2.35
B	3.0	4.6	25	120	6.87	4.99	+0.010°	1.31	+0.80
			50	4					
C	5.6[d]	1.4	25	140	3.48	1.95	+0.020°[e]	1.24	+0.63
			50	4					
D	4.0	12.1	25	432	6.80	0.65	+0.015°[f]	5.40	+0.77
E	3.9	12.5	25	288	7.45	6.70	~0	—	—
F	4.0	11.5	25	216	9.44	6.50	~0	—	—
G	4.0	9.3	25	320	2.79	1.04	~0[g]	0.75	+0.55
			90	41					

[a] l = 1 dm.; homogeneous if not otherwise stated.
[b] w_i = weight of the polymer fraction having $\{[\alpha]_D\}_i$.
[c] At 350 mμ α^{20} (l = 1 dm.) = +0.045° (c = 3.75, methanol).
[d] $TiCl_4$ instead of $TiCl_3$ was used.
[e] Unchanged after bromination by Br_2 at 0°C.
[f] l = 0.5 dm.; c = 13.2 in methanol.
[g] l = 1 dm.; c = 20.0 in methanol.

In order to check if one enantiomer is preferentially polymerized by the optically active catalyst, in one series of experiments we recovered the unpolymerized monomer (Table IV) and measured its optical activity. In most experiments the recovered olefin was optically inactive, and only in few cases was a very small positive optical rotation found.

According to the sign of the rotation of (*S*)-4-methyl-1-hexene (Table V), this small positive optical rotation might be taken as an indication that (*S*)-4-methyl-1-hexene was preferentially polymerized by the optically active initiator having the (*S*) absolute configuration.

TABLE V
Optical Rotation of Some Hydrocarbons and their Derivatives Having (*S*) Absolute Configuration

Compound	$[\alpha]_D$	Temp., °C.	Ref.
(*S*)-3-Methylhexane	+10.1°	25	Levene and Marker[20]
(*S*)-4-Methyl-1-hexene	−2.8°	25	Pino et al.[21]
(*S*)-1,2-Dibromo-4-methylhexane	+11.5°	25	Lardicci and Conti[22]
(*3S*:*6S*)-3,6-Dimethyloctane	+19.5°	20	Pino and Lardicci[23]

As the unpolymerized monomer was recovered by distillation from the polymerization mixture by azeotropic distillation with methanol, the positive optical rotation could also be due to traces of (3*S*:6*S*)-3,6-dimethyloctane which is known[3] to be formed in the decomposition of the tris-[(*S*)-2-methylbutyl]aluminum. To determine whether the optical activity should be attributed to the monomer or to other impurities, the monomer recovered from experiments C and M has been converted in the dibromide, which has an opposite optical rotation with respect to the olefin (Table V). In both cases the optical activity remained unchanged after bromination, showing that the optical activity could not be attributed to the recovered monomer.

In fact, the 4-methyl-1-hexene regenerated from the purified dibromide was optically inactive, showing that the polymerization rate difference between the two enantiomers, if any, is very small, at least under the experimental conditions used.

In Table VI we report the optical activity of the polymers obtained by catalysts prepared from different optically active organometallic compounds. No marked difference has been found using tris-[(*S*)-4-methylhexyl]aluminum in the place of tris-[(*S*)-2-methylbutyl]aluminum diethyl etherate. On the contrary, with a (*R*)-1-lithium-2-methylbutane catalyst a polymer having a much lower optical activity has been obtained.

The reaction product of $TiCl_4$ with ZnR_2, which in the case of propylene appears to be a rather poor polymerization catalyst,[4] can be successfully used in the polymerization of 4-methyl-1-hexene. The polymers thus obtained have been fractionated by solvent extraction, and atactic, block, and isotactic polymers were obtained. The $\bar{M}_v$ of the different fractions are remarkably smaller than those of the corresponding fractions obtained by

TABLE VI

Optical Activity in Hydrocarbon Solution of Fractions of Poly-4-methyl-1-hexene Obtained by Polymerization of the Racemic Monomer in the Presence of Catalytic Systems Prepared from Different Optically Active Organometallic Compounds and $TiCl_3$ (ARA) or $TiCl_4$

		Acetone-soluble fraction			Acetone-insoluble diethyl ether-soluble fraction				Diethyl ether-insoluble, isooctane-soluble fraction			
Run	Catalyst	%	α_D^{20} (l = 1 dm.)	$[\alpha]_D^{20}$	%	α_D^{20} (l = 1 dm.)	$[\alpha]_D^{20}$	$[\eta]$, dl./g.[a]	%	α_D^{60} (l = 1 dm.)	$[\alpha]_D^{20}$	$[\eta]$, dl./g.[a]
H	(*R*)-2-Methylbutyl-lithium/$TiCl_4$	57.4	+0.015°	+0.7°	37.6	+0.010°	+0.6°	0.15	5.0	—	—	—
L	Bis-[(*S*)-2-methylbutyl]-zinc/$TiCl_4$	31.7	+0.295°	+13.6°	31.3	+0.035°	+2.3°	0.09	37.0	+0.040°	+2.2°	0.36
M	Tris-[(*S*)-4-methylhexyl]-aluminum/$TiCl_3$	21.0	+0.075°	+4.6°	47.5	+0.030°	+3.1°	0.29	31.5	~0	~0	5.40

[a] Determined at 120°C. in tetralin.

$TiCl_4/AlR_3$ catalysts. These results are in good agreement with those of Natta et al.[5] showing $\bar{M}_v$ lowering caused by ZnR_2 in the propylene polymerization.

The optical activity of the fractions of poly-4-methyl-1-hexene obtained by $TiCl_4/Zn(i\text{-}C_5H_{11})_2$ catalyst is remarkably high; a careful fractionation in five fractions having different stereoregularity (Table VII) shows that the optical rotation does not decrease regularly with increasing $\bar{M}_v$.

TABLE VII

Optical Activity in Hydrocarbon Solution of Fractions of Poly-4-methyl-1-hexene Obtained by Polymerization of the Racemic Monomer in the Presence of Bis-[(*S*)-2-methylbutyl]-zinc and $TiCl_4$ (Run N)

Fraction	%	α_D (l = 1 dm.)[a]	$[\alpha]_D$[a]	$[\eta]$, dl./g.[b]
Acetone-soluble	30.2	+1.385°	+15.2°	[c]
Acetone-insoluble, ethyl acetate-soluble	20.0	+0.150°	+4.4°	0.10
Ethyl acetate-insoluble, diethyl ether-soluble	11.8	+0.040°	+4.1°	0.21
Diethyl ether-insoluble, diisopropyl ether-soluble	5.1	+0.065°	+4.8°	0.32
Diisopropyl ether-insoluble, isooctane-soluble	32.9	+0.030°	+1.7°	0.87

[a] Determined at 20°C. for the acetone-soluble and for the acetone-insoluble, diethyl ether-soluble fraction; at 50°C. for the other fractions.

[b] At 120°C. in tetralin.

[c] Molecular weight determined by cryoscopy in benzene: 750 ± 50.

Despite the high optical activity of the poly-4-methyl-1-hexene obtained by $TiCl_4/ZnR_2$ catalyst, the recovered monomer did not show a measurable optical activity (Table VIII), showing that even in this case the polymerization rate of the two enantiomers is not remarkably different.

DISCUSSION

Some fractions of polypropylene and of polystyrene obtained by catalysts prepared from transition metals compounds and organometallic compounds which contain (*S*)-2-methylbutyl groups, having rather high optical purity (90–95%), show a low optical activity confirming our preliminary data.[6] Murahashi, Nozakura, and Takeuchi,[7] polymerizing styrene by catalysts prepared from optically active tris-[(*S*)-2-methylbutyl]-aluminum and $TiCl_3$, and Fray and Robinson,[8] polymerizing propylene with catalysts prepared from optically active tris-[2-methylpentyl]aluminum and $TiCl_3$, did not find optical activity in the polymers. The discrepancy between the results of the above authors and our results, can be mainly attributed to the different optical purity of the aluminum alkyls used, to the different aluminum alkyls/olefin ratio used, and, in some cases, to the different reaction temperature adopted.

TABLE VIII

Polymerization of (*R*)(*S*)-4-Methyl-1-hexene in the Presence of Different Optically Active Organometallic Compounds and $TiCl_3$ or $TiCl_4$

Polymerization conditions					Initial	Unpolymerized monomer		Polymer	
Run	MeR_n moles/ mole $Till_n$	Olefin, moles/ mole MeR_n	Temp., °C.	Duration, hr.	monomer, g.	Weight, g.	α_D^{20}	Weight, g.	$\Sigma_i\{[\alpha]_D\}_i w_i$[a]
H	2.0	1.5	25	16	1.40	—	–	0.10	+0.13
L	21.4	7.2	25	46	2.10	—	+0.005°[b]	0.48	+2.80
			40–45	20					
M	8.8	26.9	0	13	4.86	4.40	~0[c]	0.31	+0.74
N	8.8	12.0	25	136	3.48	0.49	~0[d]	1.08	+7.35
			50	8					

[a] w_i = weight of the polymer fraction having $\{[\alpha]_D\}_i$.

[b] l = 1 dm. At 350 mμ α^{20} (l = 1 dm.) = +0.045°. In both cases, the optical activity measurements were carried out on an isooctane solution of the unpurified monomer (c not determined).

[c] Determined at 380 mμ, l = 0.5 dm. (c = 31.4, diethyl ether). The unpurified monomer had shown α_D^{20} (l = 1 dm.) = +0.43°.

[d] Determined on the unpurified monomer; l = 2 dm. (c = 5.9, isooctane), at 350 mμ α^{20} (l = 1 dm.) = + 0.400°.

In fact, as the optical activity arising from the asymmetric carbon atoms of the principal chain of both isotactic and atactic vinyl polymers should be vanishingly small owing to internal compensation,[9] the optical activity of polypropylene and polystyrene should arise only from the presence of optically active endgroups initially bound to the aluminum alkyls.[10]

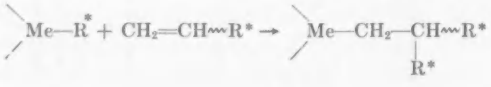
Only in the case of the acetone-extractable polymers, which generally are not completely linear head-to-tail polymers, can the presence of more than one optically active group for each molecule be reasonably conceived* according to the current views on the mechanism of stereospecific polymerization.

Owing to chain transfer with the monomer, at high monomer concentration the number of chains initiated by the alkyl groups originally bound to the aluminum atom can be rather small; on the contrary, with very low concentration of monomer and with rather high aluminum-alkyl/monomer ratio, the number of macromolecules initiated by optically active groups appears to be sufficient to give rise to an appreciable optical activity, not only in the low molecular weight acetone soluble polymers but also in the acetone-insoluble, ethyl acetate-soluble and in the ethyl acetate-insoluble, diethyl ether-soluble fractions having a relatively high $\bar{M}_v$ (Table I) and a substantially linear head-to-tail structure.

According to the origin of the optical activity in the polymers we have prepared, the values of the rotatory power do not seem to be remarkably dependent on the stereoregularity of the polymers, but they depend mainly on the $\bar{M}_v$ of the fractions, being higher in the low molecular weight fractions than in the high molecular weight ones.

The concentration of the optically active 2-methylbutyl endgroups both in the polypropylene and in the polystyrene cannot be calculated exactly, owing to the lack of knowledge on the molecular weight distribution in the fractions we have considered, and on the rate of the different chain transfer processes. Therefore we can not discuss in detail at the present the possible increase of the rotation of the 2-methylbutyl endgroups connected with the existence of particular conformations of the terminal section of the polymer principal chains or with a possible asymmetric induction of the asymmetric carbon atom of the terminal group on the formation of the next asymmetric carbon atom of the principal chain.

* If in the acetone-extractable polymers there are present some vinyl double bonds arising, for instance, from an occasional head-to-head enchainment of monomeric units followed by a chain transfer reaction, these molecules could react with a Me–R* bond, R* being an optically active group. By this reaction a nonterminal optically active isoamyl group can be inserted in a polymer molecule which might already contain a terminal R* group:



In any case, the $\bar{M}_v$-dependent optical activity of polypropylene and polystyrene which should be related to the presence in the polymers of the optically active groups originally bound to the aluminum or lithium, confirms the original interpretation of the mechanism of the stereospecific polymerization of the α-olefins.[10]

The poly-4-methyl-1-hexene obtained from the racemic monomer by catalyst prepared from optically active organometallic compounds, has an optical activity which is comparable to that observed in the polystyrene and polypropylene obtained by the same catalysts, and is 10 to 100 times lower than the absolute value of the optical activity of the poly-(*S*)-4-methyl-1-hexene samples having comparable stereoregularity.[11]

The above results and the not measurable optical rotation in the recovered monomer can be in principle interpreted by two opposite hypotheses: (1) the type of enantiomer which prevails in a macromolecule is determined by the absolute structure of the endgroups but, owing to a very rapid chain transfer process with the monomer, only very few macromolecules (about 0.5–10%) are initiated by the optically active groups originally present in the organometallic compound; (2) most of the macromolecules are initiated by optically active groups originally bound to a metal atom of the catalyst, but the absolute configuration of the terminal groups does not determine the type of enantiomer which is preferentially chosen[6] to build up each macromolecule.

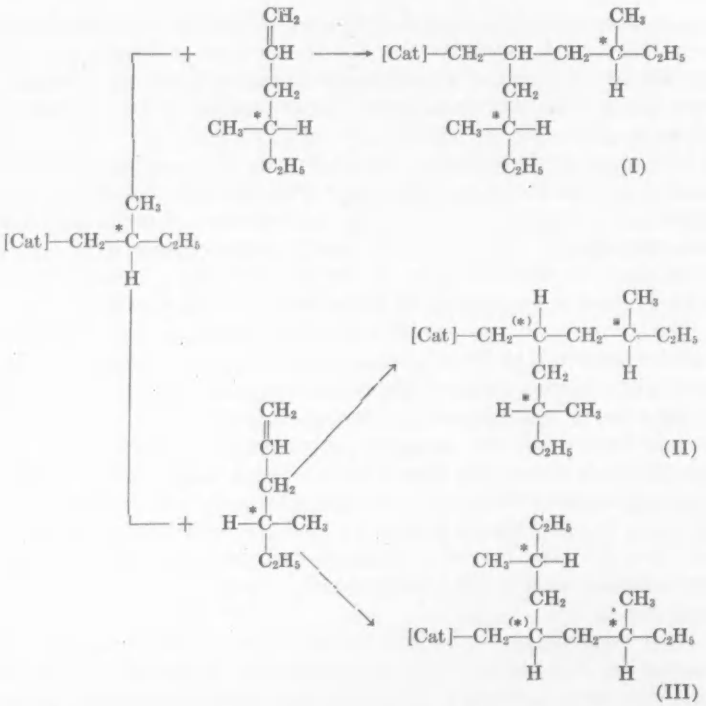
In our opinion, on the basis of the knowledge on the stereospecific polymerization of α-olefins,[2,10,12] and particularly on the polymerization of propylene in the presence of zinc alkyls,[5] and taking into account the results we have obtained in the polymerization of styrene and propylene by optically active initiators, an extremely low content of optically active end groups in the polymer, should be excluded particularly in the case of poly-4-methyl-1-hexene obtained by $TiCl_4/Zn(i\text{-}C_5H_{11})_2$ catalyst.

Furthermore preliminary chromatographic analyses (carried out with the collaboration of Dr. G. Montagnoli) of the acetone-extractable polymers of run N using (+)-poly-(*S*)-3-methyl-1-pentene as support have demonstrated that the optical activity is not concentrated in the last fractions as should be expected if the optical activity, according to the first hypothesis, were to be related only to the presence in the acetone-extractable polymers of small quantities of acetone soluble poly-(*S*)-4-methyl-1-hexene.

The most likely explanation for our experimental data, at the present stage of our research, can be given by assuming that the endgroups can not determine the type of enantiomer which will be preferentially chosen to build up each single macromolecule.

The remarkably high optical activity of the poly-4-methyl-1-hexene fractions obtained from $Zn(i\text{-}C_5H_{11})_2/TiCl_4$ catalysts can not be explained only on the basis of the presence of optically active endgroups.

If the initiation of the polymer chain by $Zn(i\text{-}C_5H_{11})_2/TiCl_4$ catalyst occurs according to the scheme:



where *C is an asymmetric carbon atom and $^{(*)}$C is a pseudoasymmetric carbon atom, the high values of the optical rotation could be explained at least in part supposing that, owing to asymmetric induction by the terminal (*S*)-2-methylbutyl group, the endgroup (I), which should have a molar optical rotation calculated by the Brewster method[24] of +70°, largely prevails.

In this case an excess of (*R*)-4-methyl-1-hexene should be present in the recovered monomer but, as this excess would be proportional to the organometallic compounds consumed during the polymerization, in our experiments it would be too small to be detected by polarimetric methods.

If groups of the type (I) are included in the first isotactic section of the macromolecule, a further exaltation of the optical activity can be foreseen on the basis of our preceding research on poly-(*S*)-4-methyl-1-hexene,[11] and in this way also the relatively high rotation of the ether-insoluble poly-4-methyl-1-hexene fractions can be reasonably explained.

EXPERIMENTAL

Materials

α-Olefins. Racemic 4-methyl-1-hexene was prepared and purified as already described.[13] Propylene was distilled in the presence of metallic

Na immediately before use. Commercial styrene was purified by distillation at reduced pressure.

Catalysts. (*R*)-2-methylbutyllithium[14] (optical purity 96–97%), and tris-[(*S*)-2-methylbutyl]aluminum diethyl etherate[15] (optical purity 91%) were prepared according to the methods described in the literature. Tris-[(*S*)-4-methylhexyl]aluminum, b.p. 150°C./0.4 mm. Hg, $[\alpha]_D^{18}$ + 18.4° (c = 7.59 in racemic 4-methyl-1-hexene) was obtained by reacting triisobutylaluminum (kindly supplied by the Montecatini Co.) with (*S*)-4-methyl-1-hexene, n_D^{25} 1.3976, $[\alpha]_D^{25}$ −2.83° (optical purity 93%) in the presence of Ni acetylacetonate as a catalyst.[16] The synthesis of bis-[(*S*)-2-methylbutyl]zinc, $[\alpha]_D^{25}$ +9.93° (homog.) shall be described elsewhere.[17] We are indebted to Dr. L. Lardicci for this sample of (+)bis-[(*S*)-2-methylbutyl]zinc. With the only exception of (*R*)-2-methylbutyllithium, which was used in light petroleum solution, all the above organometallic compounds were purified by distillation at reduced pressure immediately before use. Commercial $TiCl_4$ without further purification and, with the exception of run M (Tables VI and VIII), in which ARA $TiCl_3$ was employed, α-$TiCl_3$ were used to prepare the catalysts.

Polymerization Experiments

Polymerization of (*R*)(*S*)-4-Methyl-1-hexene. The experiments were carried out in glass sealed tubes under nitrogen. Isooctane was used as solvent in runs L and N (Tables VI–VIII). The reactions were stopped by decomposing the catalyst by adding a large excess of pure methanol to the polymerizing mixture.

In order to recover the unpolymerized olefin, the decomposition was followed by a fractional distillation which afforded the azeotropic olefin–methanol mixture. The alcohol was removed by treatment with water and drying was performed by $CaCl_2$. The obtained polymer was purified as previously reported.[13]

In run M (Tables VI and VIII), to 0.032 g. (0.0002 moles) of $TiCl_3$ were added at 0°C. 0.5965 g. (0.0018 moles) of tris-[(*S*)-4-methylhexyl]aluminum and 4.86 g. (0.0496 moles) of (*R*) (*S*)-4-methyl-1-hexene. The polymerization was carried at 0°C. for 13 hr.; the weight of polymer obtained was 0.305 g. (yield 6.5%).

4.4 g. of unpolymerized hydrocarbons having n_D^{20} 1.3992, α_D^{20} (l = 1 dm.) + 0.43° and an olefin content of 70% (determined by bromination) were recovered. The olefin was separated from this mixture by addition of bromine at −16°C. and distillation under reduced pressure of the obtained dibromide. A diethyl ether solution (c = 31.4 g./100 ml.) of the olefin regenerated, n_D^{25} 1.3978, by treatment of the 1,2-dibromo-4-methylhexane with zinc in ethanol, did not show optical activity in a 0.5 dm. tube at 380 mμ.

Polymerization of Styrene. In the first run (Table II), 1.36 g. (0.0130 moles) of styrene, n_D^{25} 1.5440, was added at −78°C. to 0.0019 moles of

(*R*)-2-methylbutyllithium dissolved in 1 ml. of petroleum ether. After 18 hr. at −78°C. the catalyst was decomposed; 1.29 g. of dry polymer was obtained (yield, 94.8%).

In the second run, 0.072 g. (0.0002 moles) of chromium tris-acetylacetonate (CrA_3, kindly supplied by Prof. L. Porri of the Institute of Industrial Chemistry of Milan Polytechnic) was dissolved in 10 ml. of anhydrous toluene containing 3.26 g. (0.0313 moles) of freshly distilled styrene, n_D^{25} 1.5440, and, after cooling at −78°C., 0.0031 moles of (*R*)-2-methylbutyllithium in 1.9 ml. of petroleum ether were added. The mixture was maintained at −78°C. for approximately 46 hr. and then at 20–25°C. for 42 hr. After this period of time, the polymerization was stopped by adding 5 ml. of methanol and the obtained polymer was purified and dried to constant weight. The yield was 3.22 g. (98.9%).

Polymerization of Propylene. In run A (Table I), propylene was passed for approximately 10 hr. into a mixture of 0.55 g. (0.0036 moles) of α-$TiCl_3$ and 5.67 g. (0.0180 moles) of tris-[(*S*)-2-methylbutyl]aluminum diethyl etherate, $[\alpha]_D^{27}$ +23.9° (homog.), at 75–80°C.; 0.398 g. of dry polymer was obtained. In run B, the reaction was carried out in a 100 ml. autoclave with the use of 8.24 g. (0.0262 moles) of tris-[(*S*)-2-methylbutyl]aluminum diethyl etherate, $[\alpha]_D^{25}$ +22.1° (c = 5.88, isooctane) and 0.5 g. (0.026 moles) of $TiCl_4$. At a constant propylene pressure (ca. 10 atm.), 7.73 g. of polypropylene was obtained after 3 hr. at 60°C.

Characterization of the Polymers

Fractionation by Extraction with Boiling Solvents. The crude polymers were fractionated by extraction with boiling solvents, under nitrogen, using Kumagawa extractors, as described in a preceding paper.[11]

Intrinsic Viscosity. Intrinsic viscosity was determined by using a Desreux-Bischoff dilution viscometer as previously reported.[13]

Optical Activity. The determinations of optical activity at 589.3 mμ were carried out by using an apparatus previously described.[11] The measurements at shorter wavelengths were carried out with the use of a Rudolph photoelectric spectropolarimeter, model 200 S.

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Synopsis

The polymerization of racemic 4-methyl-1-hexene by catalysts prepared from $TiCl_4$ or $TiCl_3$ and (+)tris-[(*S*)-2-methylbutyl]aluminum diethyl etherate, (+)tris-[(*S*)-4-methylhexyl]aluminum, (+)bis-[(*S*)-2-methylbutyl]zinc, and (+)(*R*)-2-methylbutyllithium has been investigated. The polymer obtained was fractionated by solvent extraction; the low molecular weight fractions have a rather low optical activity which cannot, however, be entirely accounted by the presence of the optically active end groups. Similar results have been obtained on polymerizing propylene and styrene in the presence of optically active organometallic compounds, but in this case, the optical activity is lower and can be reasonably accounted by the presence of optically active end groups in the polymer molecules. The above results indicate that in the polymerization of racemic 4-methyl-1-hexene the presence of optically active groups initially bound to the catalyst is not sufficient to hinder appreciably the polymerization of one of the two enantiomers, the asymmetric induction being probably restricted to the addition of the first monomeric units.

Résumé

On a étudié la polymérisation du 4-méthyl-1-hexène racémique au moyen de catalyseurs préparés à partir de $TiCl_4$ ou $TiCl_3$ et de (+)tris-((*S*)-2-méthyl-butyl)aluminium diéthyle éthérate, de (+)tris-((*S*)-4-méthyl-hexyl)-aluminium, de (+)-bis-((*S*)-2-méthyl-butyl)-zinc et de (+)(*R*)-2-méthyl-butyl-lithium. Le polymère obtenu a été fractionné par extraction aux solvants. Les fractions de faible poids moléculaire ont une activité optique un peu plus faible, ce qui ne peut cependant pas être entièrement attribuée à la présence de groupements terminaux optiquement actifs. Des résultats semblables ont été obtenus lors de la polymérisation du propylène et du styrène en présence de composés organométalliques optiquement actifs. Mais dans ce cas, l'activité optique est plus faible et peut raisonnablement être attribuée à la présence de groupements terminaux optiquement actifs dans les molécules de polymères. Les résultats ci-dessus montrent que lors de la polymérisation du 4-méthyl-1-hexène racémique, la présence de groupements optiquement actifs liés initialement au catalyseur ne suffit pas à empêcher d'une façon appréciable la polymérisation d'un ou de deux énantiomères, l'induction asymétrique étant probablement réduite à l'addition de la première des unités monomériques.

Zusammenfassung

Die Polymerisation von razemischem 4-Methyl-1-hexen mit Katalysatoren aus $TiCl_4$ oder $TiCl_3$ und (+)Tris-[(*S*)-2-methyl-butyl]-aluminium-diäthylätherat, (+)Tris-[(*S*)-4-methyl-hexyl]-aluminium, (+)Bis-[(*S*)-2-methyl-butyl]-zink und (+)(*R*)-2-Methyl-butyl-lithium wurde untersucht. Das erhaltene Polymere wurde durch Lösungsmittelextraktion fraktioniert; die niedermolekularen Fraktionen besitzen eine ziemlich geringe optische Aktivität, die aber doch nicht zur Gänze durch die Anwesenheit der optisch aktiven Endgruppen erklärt werden kann. Ähnliche Ergebnisse wurden bei der Polymerisation von Propylen und Styrol in Gegenwart optisch aktiver, organometallischer Verbindungen erhalten; in diesem Fall ist aber die optische Aktivität niedriger und lässt sich durch die Anwesenheit der optisch aktiven Endgruppen in den Polymermolekülen befriedigend erklären. Die angeführten Ergebnisse zeigen, dass bei der Polymerisation von razemischem 4-Methyl-1-hexen das Vorhandensein der anfänglich an den Katalysator gebundenen optisch aktiven Gruppen zu einer stärkeren Behinderung der Polymerisation eines der beiden Enantiomeren nicht ausreicht, da die asymmetrische Induktion wahrscheinlich auf die Addition der ersten Monomereinheiten beschränkt ist.

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Kinetic Study of the Heterogeneous Polymerization of Styrene and/or α-*d*-Styrene by Ziegler-Natta Catalysis

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I. INTRODUCTION

The general mechanism for heterogeneous Ziegler-Natta catalysis, using TiX_3 or TiX_4 and AlR_3 (where X is halogen and R is alkyl), as proposed by Natta[1] locates the point of attachment of the growing polymer chain on the beta carbon of the monomer for propylene. It is probable that the polymerization of styrene will, under similar experimental conditions, occur in a similar fashion, i.e., on the beta carbon, but there are good reasons to believe that this may only partially be true. Changes of the experimental conditions producing changes in the nature of the catalyst[1] may also change the mode of propagation for a given monomer.[2] Termination reactions for polypropylene formation have been extensively studied by Natta[1] and shown to involve monomer, catalyst, and/or the growing polymer chain. In these reactions it was indicated that hydride ion abstraction takes place at the alpha carbon. Termination reactions for Ziegler-Natta catalysis involving monomers other than propylene remain as yet ill defined.

Based on the above discussed data, α-*d*-styrene was chosen for the study of heterogeneous Ziegler-Natta catalysis. Advantage is taken of the well known isotope effect of hydrogen vs. deuterium in general organic reactions involving proton and to a lesser extent hydride ion transfer or abstraction. It was hoped that deuteration of the alpha carbon may shed light on the termination reaction(s) involved, if, indeed they occur at the alpha position. Deuteration of the alpha position may also affect the rate and/or mechanism of the propagation reaction, as has been indicated for the free radical polymerization of allyl-1-d_2-acetate.[3] A change of substituent at the alpha position may affect the mode of coordination and/or the stability of the resulting complex.[4]

The choice of proper operating conditions and the interpretation of data for the formation of homopolymers and copolymers of α-*d*-styrene and styrene is complicated by the fact that these monomers undergo free radical polymerization with ease. Free radicals are proposed to be generated in solution during the formation of an insoluble complex of TiX_4 and AlR_3.[1] There is some doubt, however, that these are really "free" radicals but rather adsorbed on the solid surface with the aid of the open *d*-orbitals of

the transition metal catalyst; it has been suggested that even the formation of an olefin and a paraffin from a homogeneous catalyst could take place within a complex by intramolecular diaproportionation of two alkyl groups.[5] In any event, it is likely that by the choice of proper experimental conditions one can either minimize or eliminate free radicals prior to the point of monomer introduction into the reaction vessel containing the catalyst.[6]

Attempts have been made earlier to determine the effect of deuterium substitution at the alpha position on per cent conversion and intrinsic viscosities of the resulting polymer, using *α-d*-vinyl-cyclohexane and heterogeneous Ziegler-Natta catalysis.[7] No effect of deuterium at the alpha position on intrinsic viscosities and conversion was noted.

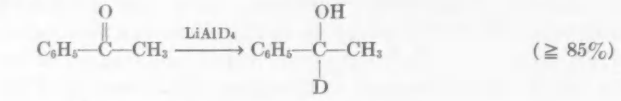
Tetradeuterated ethylene polymerized by heterogeneous Ziegler-Natta catalysis showed no intrinsic viscosity increase compared to that determined for ethylene.[8]

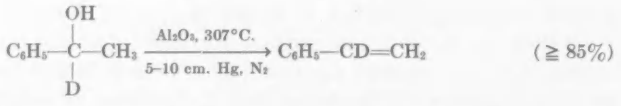
To clarify all of the above quoted data a kinetic study of the polymerization of *α-d*-styrene and/or styrene by heterogeneous Ziegler-Natta catalysis has been instituted. Since an "isotope effect" should be operative based on the present day knowledge of the propagation and/or termination reactions in heterogeneous Ziegler-Natta catalysis, only an evaluation of the reaction rate constants could explain the apparent lack of dependence of polymer intrinsic viscosities on deuteration of the monomer.

II. EXPERIMENTAL

1. Preparation of *α-d*-Styrene

The *α-d*-styrene monomer was successfully prepared by using a method based on that reported by Wall and Brown,[9] i.e., by a general procedure involving the reactions:





The *α-d*-styrene content was determined by a combination of mass spectroscopy and nuclear magnetic resonance. The above procedure resulted in 100%, 81.5%, and 89.5% pure *α-d*-styrene for three attempts, the remainder being styrene and trace amounts of di- and trideuterated styrene.

a. 1-Phenylethanol-1-*d* (I). To a solution of 5.2 g. (0.124 mole) $LiAlD_4$ in 300 ml. of absolute ethyl ether are added dropwise 44.4 g. (0.37 mole) of redistilled acetophenone in ca. 100 ml. of absolute ethyl ether. Upon completion of the addition, the mixture was refluxed for an additional 20 hr. and then decomposed with 100 ml. of water. The resulting slurry containing

the hydroxides was "titrated" with dilute H_2SO_4 until two clear layers resulted. The ether layer was separated and the water layer was discarded. The ether was evaporated on a rotary evaporator and the residual oil distilled through a Vigreaux column yielding 39.4 g. of product I (87%), b.p. 79°C. (2.3 mm.), $n^{24} = 1.5267$.

b. α-*d*-Styrene (II). 1-Phenylethanol-1-*d*, 34.5 g. (0.28 mole), I, was pyrolyzed over Al_2O_3 which was predried at ca. 120°C. (10 cm. Hg) overnight. The column (1 in. diam.) was packed with the predried alumina to a height of 1 ft., brought to temperature (307°C.) while maintaining a 10 cm. Hg vacuum and a nitrogen flow rate of ca. 30 bubbles/min. I was added dropwise (30 drops/min.) to the column, and the pyrolyzate collected in a Dry Ice–acetone cooled flask. The pyrolyzate was distilled through a Vigreaux column to yield 27.0 g. (0.26 mole, 92%), b.p. 81.5°C. (10 cm. Hg) of II. The product II was redistilled through a Vigreaux column at 76°C. (8.2 cm. Hg) to yield 24.2 g. of II. The α-*d*-styrene was shown to be 100% pure by mass spectroscopy and NMR, $d^{20} = 0.9118$, $n^{24} = 1.5435$.

2. Dilatometric Apparatus and Technique

a. Purification of Benzene (Solvent). Reagent grade benzene obtained from the Brothers' Chemical Co. of New Jersey was extracted twice with

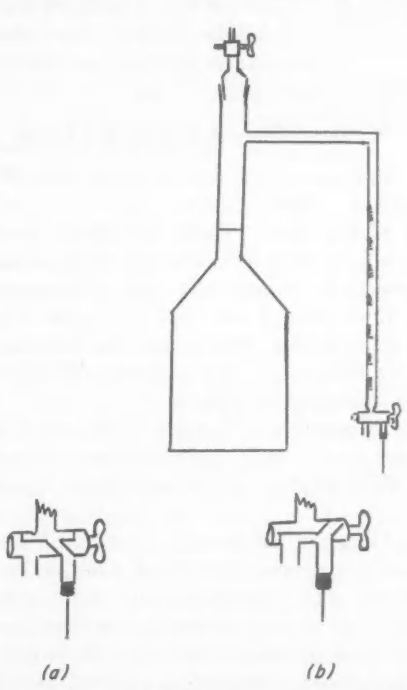


Fig. 1. Catalyst delivery system. (*a*) Delivery position, (*b*) nitrogen purge position.

concentrated sulfuric acid. The benzene was then washed twice with approximately 10% solution of sodium bicarbonate in water and then twice with water. The benzene was then stored overnight over anhydrous sodium sulfate and then distilled over calcium hydride. The benzene was stored over calcium hydride.

b. Preparation of Catalyst Solutions. Standard solutions of titanium tetrachloride and triethyl aluminum in purified and distilled benzene were prepared as follows: (1) distillation of the "as is" material into preweighed ampules; (2) determination of ampule glass and content weight; (3) insertion of ampules into the catalyst delivery apparatus shown in Figure 1, in an inert atmosphere; (4) covering of ampules with solvent prior to breaking them under the solvent in an inert atmosphere. The liquid level was adjusted with additional solvent to the mark of the volumetric flask.

Using a density of 2.23 g./cm.^{3} for Pyrex glass, the formalities of the prepared solutions were calculated, by this method as a 0.276F solution of titanium tetrachloride in benzene, using titanium tetrachloride distilled at 74.5°C. (10.8 cm. Hg) and a 0.295F solution of triethylaluminum in benzene, using triethylaluminum distilled at 140°C. (9.8 cm.). The catalyst delivery system is designed in such a way (as shown in Fig. 1), that measured amounts of the solution can be delivered to the reaction flask through a syringe needle. This method of delivery excludes water and oxygen from the surroundings. The delivery tip is designed so that a quantitative delivery can be made by blowing out the syringe needle after reading the final volume on the buret.

3. Measurements of Reaction Rates

A drawing of the apparatus employed is shown in Figure 2. The process involves a series of distinct steps.

a. Pretreatment of Apparatus. Bringing of the glassware in the oil bath to the desired temperature was followed by a series of alternating evacuations and N_2 admissions, to insure an inert atmosphere. The vacuum obtained in these runs varied from 0.5 to 10^{-4} mm. Hg. Although the actual vacuum obtained in these runs varied, it is felt that repeated evacuations followed by readmissions of dry nitrogen at 60°C. was as effective as a single evacuation at a higher vacuum.

b. Charging the Monomer(s). Stopcocks A and B in Figure 2 were closed and monomer was syringed into the sidearm through the serum cap. Some solvent was added at this stage so as to reduce transfer error into the reaction flask later.

c. Preparation of Catalyst. Stopcock C in Figure 2 was now closed, and a measured volume of titanium tetrachloride solution was injected via the addition funnel serum cap. The remaining volume of necessary benzene for the run was used now to wash down the addition funnel. A measured volume of triethylaluminum solution was injected through the serum cap of the addition funnel and added dropwise to a stirred solution of the titanium tetrachloride in benzene, so as to minimize changes in temperature. The

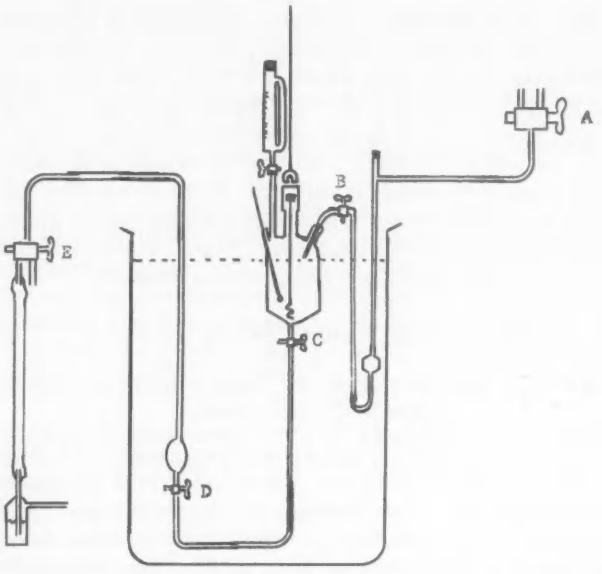


Fig. 2. Monomer-solvent–catalyst mixing chamber and dilatometer.

finely divided heterogeneous catalyst system was now allowed to come to equilibrium, while stirring was continued for the remainder of the run.

d. Addition of Monomer to Catalyst. With a slight nitrogen pressure through stopcock A, the monomer was transferred into the catalyst by opening stopcock B. When transfer was complete, stopcock B was closed. Time of this transfer was held constant and was approximately 20 min. after the completion of the preparation of the catalyst solution. Occasional venting of the reaction flask with a syringe needle avoided pressure build-up in the flask at this point.

e. Transfer of Reaction Mixture into Dilatometer. The transfer was made about 2 min. after the introduction of monomer. A bleed needle was introduced into the serum cap of the addition funnel with its stopcock open. Stopcock C was opened and the contents allowed to drain slowly through the connecting capillary into the dilatometer bulb and approximately $^3/_4$ of the way up the precision capillary. The rise in the precision capillary could easily be checked by closing stopcock E. When the desired height was reached, stopcock D was closed and then C. Stopcock E was opened to the Hg sink, and readings were started with the cathetometer.

f. Isolation of Polymer. After completion of the run, stopcocks D and C were opened and stopcock E was opened to the rubber bulb. By applying gentle pressure to the bulb, the reaction mixture was returned to the reaction vessel. Stopcock C was closed and the equipment dismantled. The reaction mixture was precipitated into a methanol·HCl solution.

The polymer was filtered and then washed overnight in a stirred methanol slurry. Polymer was again filtered and then dried in a vacuum oven at ca. 60°C. (10–15 cm. Hg) for approximately 12 hrs. Conversion was determined at this point. The polymer was redissolved in hot chlorobenzene and this solution was filtered through fluted filter paper to remove insoluble hydroxides, not removed initially. The actual amount of insoluble material at this point is extremely small. The polymer was very slowly reprecipitated in methanol, filtered, and redried in the vacuum oven prior to viscosity determination in chlorobenzene. Viscosities were determined by dilution of a 0.5% solution of the polymer in chlorobenzene.

III. DISCUSSION

1. Reaction Rate Measurements of Homopolystyrene Formation by Ziegler-Natta Catalysis

The technique and the apparatus involved are discussed in detail in the experimental section of this report. Homopolymers of styrene were initially prepared and their rates of formation and the intrinsic viscosities of the resulting polymers were determined at three titanium tetrachloride concentrations, all other conditions being equal. Summary of these data appears as Table I. All rate data shown in Table I, were obtained from a least square analysis of the raw data.

TABLE I
Reaction Rates for Homopolystyrene by Ziegler-Natta Catalysis[a]

$[TiCl_4]$, mole/l.	Temp., °C. (±0.05)	Time, hr.	Initial rate × 10^2, mole/l. hr.	Conversion, %	$[\eta]^{29.3}_{C_6H_5Cl}$
0.02	60.1	8.25	1.1	—	—
0.04	60.05	5.0	4.33	15	3.00
0.04	60.05	1.5	3.94	7	3.02
0.04	60.05	1.5	4.17	7	3.25
0.04	60.05	1.5	4.34	—	3.11
0.04	60.05	5.0	4.54	13	—
0.06	60.00	5.0	12.5	25	—

[a] Reaction conditions: constant $[Al(C_2H_5)_3]/[TiCl_4] = 3.0$; constant [M] = 1.02 mole/l.; average initial rate (at $[TiCl_4] = 0.04$) = 4.26×10^{-2} mole/l. hr., RMD = ±4%; $[\eta]^{29.3}_{C_6H_5Cl} = 3.10 \pm 0.09$; RMD = ±3%.

The data of Table I indicate that the initial rate of formation of homopolystyrene can be varied in this apparatus and by this technique from 1.1×10^{-2} to 12.5×10^{-2} mole/l. hr. by changing the titanium tetrachloride concentration from 0.02 to 0.06 mole/l,

The initial rate of formation of homopolystyrene can be reproduced at a single concentration of titanium tetrachloride (e.g. 0.04 mole/l.) to yield an average value of 4.26×10^{-2} mole/l. hr. with a relative mean deviation

equal to or smaller than ±4%. Also, the intrinsic viscosities of the polymers prepared at a titanium tetrachloride concentration of 0.04 mole/l. yield an average value of 3.10 ± 0.09, with a relative mean deviation (RMD) of ±3% or within the relative mean deviation of the experimental error of polymer formation.

The conclusion drawn is, that a measurement of initial rate in this heterogeneous system by means of a dilatometer, using this experimental technique and apparatus, results in reproducible initial rates of polymer formation and polymer intrinsic viscosities. It should be noted, that the per cent conversion is less than 10% at the conclusion of each run and that the rates were, therefore, measured well within the limits of accuracy in respect to the constancy of monomer concentration during the time period of these measurements. The viscosities are low enough so as to yield straight line extrapolations with relative ease.

2. Reaction Rate Measurements for Copolymers of α-*d*-Styrene and Styrene by Ziegler-Natta Catalysis

Copolymers of α-*d*-styrene and styrene were prepared with the use of varied α-*d*-styrene monomer feed concentrations at conditions which yield an average initial rate of 4.26×10^{-2} mole/l. hr. for homopolystyrene. The 81.5% pure α-*d*-styrene preparation and styrene were used for all these experiments. A summary of these data appears as Table II. All

TABLE II
Reaction Rates for Copolymerization of Styrene (M_H) and α-*d*-Styrene (M_D) by Ziegler-Natta Catalysis[a]

$[M_D] \times 10^2$, mole/l.	Time, hr.	Initial rate $\times 10^2$, mole/l. hr.	Conversion, %	$[\eta]^{29.3}_{C_6H_5Cl}$
4.11	1.5	4.96	7	2.88
8.22	2.0	5.52	7	3.03
16.44	1.5	5.56	6	3.25
24.66	1.5	6.44	9	2.80
82.20	1.5	7.50	6	3.45

[a] Reaction conditions: constant $[TiCl_4] = 0.04$ mole/l.; constant $[Al(C_2H_5)_3]/[TiCl_4] = 3.0$; constant $[M_T] = [M_H] + [M_D] = 1.02$ mole/l.; temp. 60.05°C.; average $[\eta]^{29.3}_{C_6H_5Cl} = 3.08 \pm 0.21$; RMD = ±7%.

rate data shown in Table II were obtained from a least square analysis of the raw data. A plot of α-*d*-styrene concentration in the monomer feed at a constant total monomer concentration versus initial rate of polymer formation is shown in Figure 3.

Table II indicates that increasing concentrations of α-*d*-styrene yield increasing initial rates of polymer formation. This increase appears to be linear up to approximately 0.1 mole/l. of α-*d*-styrene and results in an

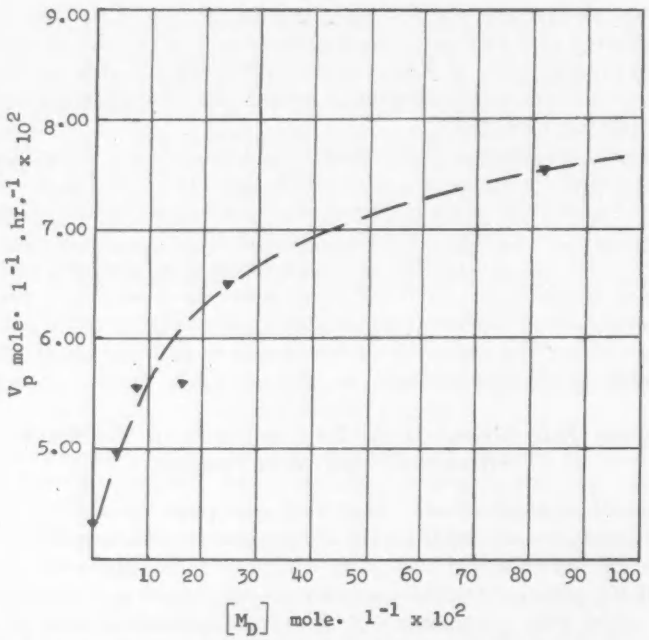


Fig. 3. Heterogeneous catalysis with $Al(C_2H_5)_3$ + $TiCl_4$ effect of α-*d*-styrene concentration on initial reaction velocity.

approximate increase of 75% over the rate of homopolystyrene formation at an α-*d*-styrene concentration of approximately 0.8 mole/l.

The intrinsic viscosities have an average value of 3.08 ± 0.21, with a relative mean deviation of ±7%. If the viscosity value of the 82.20 mole/l. α-*d*-styrene run is omitted, the intrinsic viscosity averages to 2.99 ± 0.15 with a relative mean deviation of ±4%; i.e., the relative mean deviation is reduced by almost one-half. A final conclusion cannot be reached at this point but must await more data.

3. General

An effort is made below to explain the data discussed above from a general point of view. The following is not intended to be a final analysis. The rate of polymer formation is agreed to be:

$$v_p = k_p[C^*_p][M]^n \tag{1}$$

where v_p = velocity of propagation, k_p = propagation constant, $[C^*_p]$ = concentration of active centers, $[M]$ = total monomer concentration, and n = order of reaction in respect to monomer.

There is some disagreement[10] as to whether $n = 1$ or 2, at the monomer concentration used in these experiments, but this fact will not in principle

affect the following argument. The hypothesis is made that k_p for homopolystyrene formation is equal to the k_p for the formation of a styrene–α-d-styrene copolymer; i.e., a preliminary study by infrared methods show the per cent α-d-styrene in the feed to be equal to the per cent α-d-styrene in the polymer.

It follows therefore that increases in the velocity of the propagation reaction with increases in the α-d-styrene concentration must be a function of changes in (C^*_p). This could be mathematically expressed in the following manner:

$$[C^*_p] = [C^*_0] + \alpha[M_D]^\beta \tag{2}$$

where $[C^*_p]$ = concentration of active centers during a styrene–α-d-styrene copolymerization; $[C^*_0]$ = concentration of active centers during a homopolymerization of styrene, $[M_D]$ = concentration of α-d-styrene, α = efficiency factor, and β = order of reaction in respect to α-d-styrene.

It is normally assumed that $[C^*_0]$ is independent of styrene monomer concentration, but only a function of $TiCl_4$ and $Al(C_2H_5)_3$ concentrations. The validity of this assumption has never been directly challenged in the literature, but may in the light of these data be very questionable, e.g., the production of $[C^*_0]$ itself may be a function of type and/or concentration of monomer or

$$[C^*_0] = k[Ti][Al] - \gamma[M]^\delta \tag{3}$$

Omitting the argument presented in eq. (3) and substituting $[C^*_p]$ of eq. (2) into eq. (1) yields:

$$v_p = k_p[M]([C^*_0] + \alpha[M_D]^\beta)$$

$$v_p = k_p[M][C^*_0] + \alpha k_p[M][M_D]^\beta$$

but $k_p[M][C^*_0] = v_0$, or (the velocity of homopolystyrene formation), and

$$\begin{aligned} v_p &= v_0 + \alpha k_p[M][M_D]^\beta \\ v_p - v_0 &= \alpha k_p[M][M_D]^\beta \\ \Delta v &= \alpha k_p[M][M_D]^\beta \end{aligned} \tag{4}$$

where $\Delta v = v_p - v_0$. Equation (4) is valid if n in eq. (1) is equal to unity. For all other cases eq. (1) yields:

$$\Delta v = \alpha k_p[M]^n[M_D]^\beta \tag{5}$$

It is apparent that whether eq. (4) or (5) is applicable, that at a total monomer concentration of 1 mole/l., these equations are equal. A plot of log Δv versus log $[M_D]$ yields a straight line with slope equal to $\beta = 0.5$ and with an intercept equal to $\alpha k_p[M]$; in other words, αk_p is equal to 0.039 at $[M] = 1.02$ mole/l. Equation (4) can now be rewritten in a more general form:

$$v_p = 4.26 \times 10^{-2} + 3.98 \times 10^{-2}[M][M_D]^{0.5} \tag{6}$$

It is of interest here to point out that if $[C^*_p]$ is a function of type and/or concentration of monomers used, as may well be the case, then the $[M]^2$ dependence on initial rate suggested by Burnett and Tait,[10] at low concentrations of monomers could be explained on this basis. This effect could be overridden by a mass effect so as to explain the experimental first order dependence on monomer at higher concentrations of monomer.

It was pointed out that increases of rate of propagation with increasing concentration of α-*d*-styrene appear to be a function of changes in the concentration of active centers. It was further shown that the intrinsic viscosities of polymers prepared with different initial α-*d*-styrene concentrations appear to remain constant.

The $\overline{DP}$ can be shown to be independent of $[C^*_p]$ by eq. (7):

$$\overline{DP} = \frac{v_p}{\Sigma v_t} = \frac{k_p[C^*_p][M]^n}{k_{t_1}[C^*_p] + k_{t_2}[C^*_p][M]^m + \ldots}$$

$$\overline{DP} = \frac{k_p[M]^n}{k_{t_1} + k_{t_2}[M]^m + \ldots} \tag{7}$$

Additional terms in the numerator have to date never been considered, but their existence should not be ruled out automatically. In the light of the present study, additional terms for the numerator may be possible; however, they would probably be numerically small; perhaps a more accurate statement than eq. (7) would be

$$\overline{DP} = \frac{\Sigma v_p}{\Sigma v_t} = \frac{k_{p_0}[M_0]^n + k_{p_x}[M_x]^s + \ldots}{k_{t_1} + k_{t_2}[M]^n + \ldots} \tag{8}$$

where $[M_0] \gg [M_x]$, and where the formation of M_x would be a function of type and/or concentration of $[M_0]$, $[M_0]$ being the original monomer in the systems and M_x being a monomer derived from the original by an exchange reaction at the alpha carbon.

From the above equations one can easily explain the lack of dependence of $\overline{DP}$ upon $[C^*_p]$ but must at the same time agree that (a) an isotope effect on the termination constants is either negligible or nonexistent; (b) any additional terms must not contain $[C^*_p]^n$ terms where $n > 1$ in order for the $\overline{DP}$ to remain independent of $[C^*_p]$. However, a $[C^*_p]^2$ term has been proposed for the denominator of eq. (7), although its importance has been questioned.[11]

$$\overline{DP} = \frac{k_p[C^*_p][M]}{k_{t_2}[C^*_p]^2 + k_{t_1}[C^*_p] + k_{t_2}[C^*_p][M] + \ldots}$$

$$\overline{DP} = \frac{k_p[M]}{k_{t_2}[C^*_p] + k_{t_1} + k_{t_2}[M] + \ldots} \tag{9}$$

As per eq. (9) it is no longer necessary to assume that no isotope effect is operative for the termination constants; since $[C^*_p]_D > [C^*_p]_H$, where $[C^*_p]_D$ and $[C^*_p]_H$ are active center concentrations for α-*d*-styrene and

styrene polymerization, respectively, but at the same time $(k_t)_D < (k_t)_H$ if a normal isotope effect is operative, $(k_t)_D$ and $(k_t)_H$ being termination constants for α-*d*-styrene and styrene polymerization, respectively.

These two effects may then counterbalance one another so as to produce no net change in $\overline{DP}$.

Another factor in favor of eq. (9) would be the demonstrated decreases of $\overline{DP}$ with increasing [Ti] for the Ziegler-Natta polymerization of vinylcyclohexane.[7]

These argvments do not seem unresolvable but may be settled by the proper interpretation of $1/\overline{DP}$ vs. 1/M plots. Preliminary data when plotted in this manner do not appear to exhibit a linear dependence.

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Synopsis

Initial rates of polymer formation by Ziegler-Natta catalysis [$TiCl_4$ and $Al(C_2H_5)_3$] were measured for styrene and copolymers of α-*d*-styrene and styrene. Increasing concentrations of α-*d*-styrene yield increasing initial rates of polymer formation at a constant total monomer concentration. No effect of α-*d*-styrene concentration on final polymer intrinsic viscosities was observed. The increase in the initial rate of polymer formation as a function of α-*d*-styrene concentration is believed to be the result of an increase of the concentration of active centers.

Résumé

Des vitesses initiales de formation de polymère au moyen de catalyseurs Ziegler-Natta [$TiCl_4$ et $Al(C_2H_5)_3$] ont été mesurées pour le styrène et des copolymères de l'α-*d*-styrène et du styrène. Une augmentation de concentration en α-*d*-styrène produit une augmentation de la vitesse initiale de formation du polymère à une concentration totale en monomère constante. On n'a pas observé d'influence de la concentration en α-*d*-styrène sur les viscosités intrinsèques des polymères résultants. On suggère que l'augmentation de la vitesse initiale de formation du polymère en fonction de la concentration en α-*d*-styrène est le résultat d'une augmentation de la concentration en centres actifs.

Zusammenfassung

Die Anfangsgeschwindigkeit der Polymerbildung durch Ziegler-Natta-Katalyse [$TiCl_4$ und $Al(C_2H_5)_3$] wurde an Styrol und an Copolymeren von α-*d*-Styrol und Styrol

gemessen. Steigende α-*d*-Sytrolkonzentration führt bei konstanter Totalkonzentration der Monomeren zu einer Zunahme der Anfangsgeschwindigkeit der Polymerbildung. Es wurde kein Einfluss der α-*d*-Styrolkonzentration auf die Viskositätszahl des polymeren Endproduktes beobachtet. Die Zunahme der Anfangsgeschwindigkeit der Polymerbildung als Funktion der α-*d*-Styrolkonzentration wird auf eine Zunahme der Konzentration an aktiven Zentren zurückgeführt.

Discussion

F. Danusso (*Milan, Italie*): I have two questions: (*a*) What happens to the copolymers composition, when over-all reactivity increases? (*b*) May it be suggested, as an explanation of the increased reactivity, that an exchange reaction takes place between α-*d*-styrène and phenylethyl groups (perhaps replacing original ethyl groups on the catalyst surface?

C. G. Overberger: The deuterium in the α-position of α-*d*-styrene does not effect the propagation rate as we demonstrated by copolymerization of styrene with α-*d*-styrene.

We also believe that there is an exchange reaction between monomer and active sites which destroys active sites. There are a number of possible mechanisms for this, but the evidence points very strongly to this possibility.

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The Role of Aluminum Alkyl Chlorides in Polymerization of Propylene with Titanium Chloride Catalysts

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INTRODUCTION

Continual interst has been sustained in catalysts based on titanium trichloride ever since the discovery by Natta that polypropylene of high stereoregularity can be obtained from α-$TiCl_3$ activated by metal alkyls. The success achieved by Natta's team[1a] in understanding the polymerization mechanisms owed much to the choice of triethylaluminum as activator, since a constant polymerization rate was obtained. Moreover, to avoid variations in specific activity the most important work was carried out on one particular sample of ball-milled α-$TiCl_3$; for this it was proposed that polymerization occurs on the crystal surfaces at active centers, the number of which remains constant with time. Molecular weight is then controlled by various chain-transfer processes, and average times of growth for a polymer molecule at 70°C. were found to be of the order 4–15 min., depending on concentrations of activator and catalyst. Due to transfer with activator some of the polymer no longer held by active centers was found to retain aluminum alkyl endgroups. Similar discoveries with polyethylene from other titanium catalysts were made use of by Chien[2] and by Feldman and Perry[3] to label polymer molecules with, respectively, radioactive iodine and tritium. In these systems polymer growth times of several minutes were derived.

With the use of diethylaluminum chloride as activator, polypropylene of much improved steric purity can be obtained. This high stereoregularity can be maintained at high polymerization rates by use of modified catalysts based on the violet crystalline forms of $TiCl_3$.[4] Particularly useful in this respect are compounds prepared by reduction of $TiCl_4$ with aluminum alkyls or aluminum metal which incorporate $AlCl_3$ as a solid solution in the crystal lattice. Such systems have been studied by Bier et al.[5,6] (alkyl-reduced $TiCl_4$) and by Kohn et al.[7] (aluminum metal–reduced $TiCl_4$). There is considerable doubt whether Natta's reaction schemes sufficiently describe these newer catalyst systems; this is partly due to kinetic studies being complicated by a steady fall in reaction rate as polymerization proceeds, which has been variously interpreted. Bier considers that catalyst

surfaces become starved of monomer due to diffusion control through the accumulating polymer, while Kohn, on the other hand, adopts a proposal of Patat and Sinn[8] that active centers are being lost by rearrangement of the active complex from alkyl-bridge to inactive chloride-bridge structures.

These newer catalysts are further claimed by Bier and by Kontos et al.[9] to differ greatly from Natta's in allowing each polymer molecule to grow for a very long time (15 hr. or more at 50°C.),[6] since transfer reactions are said to be negligible at normal polymerization temperatures. These conclusions are based on the observation that plots of polymerization rate or polymer reduced solution viscosity (as a measure of molecular weight) against propylene polymerized are not affected by interruption of polymerization by removal of monomer for long periods of time; reaction can be continued whenever monomer is reintroduced. If transfer processes are much rarer in these systems, the chances of formation of block copolymers by alternating introduction of two or more monomers is much increased with the possibility of producing polymer with special properties.

In the present paper a natural explanation of fall-off in polymerization rate is proposed which can be linked quantitatively to a novel reaction of activator. A study of kinetics including molecular weight growth is interpreted in terms of a simple working model, and the resemblance of these systems to those studied by Natta is shown to be closer than some previous workers have supposed. An explanation is offered for the fact that many compounds, such as ethers, amines, alkali metal halides, can increase activity without detriment to the stereoregulation.

EXPERIMENTAL

Polymerization Equipment

Laboratory-scale polymerizations were carried out at atmospheric pressure in stirred 2-liter flasks with complete exclusion of moisture and air. Monomer was fed through pressure-regulating equipment from steel burets with sight glasses through which the level of liquid propylene could be followed to within ±0.1 g. as it evaporated, the flask pressure being kept at 760 ± 2 mm. Hg. A purified saturated petroleum fraction of boiling range 175–200°C. was used as diluent, exerting a negligible vapor pressure at the temperature of polymerization. The flasks were immersed in water baths which were adjusted to keep the polymerization temperatures to within ±0.2°C.

Steel autoclaves with stirrers were available for higher pressures, and a 20-gal. polymerization vessel was found convenient for runs during which 1-liter samples were removed for analysis without disturbing the main bulk of polymerization.

Subsidiary tests demonstrated that agitation was sufficient to ensure that the rate of diffusion of propylene through the slurry was much too fast to affect the rate of polymerization.

Procedure

Vessels were charged with diluent, vacuum degassed at polymerization temperature, and saturated with propylene. Alkyls were conveniently introduced through rubber seals by means of Cornwall hypodermic syringes as 25% solutions in diluent. Catalysts were handled as slurries in diluent and were added in similar manner. Alkyls and catalysts were stored under high purity argon or nitrogen.

Polymerization was timed from introduction of catalyst, and consumption of propylene noted at frequent intervals. Polymerization rates were deduced from plots of monomer polymerized against time which were sufficiently accurate for the slow changes in rate to be followed. When required, polymerization was arrested by evacuation of monomer and replacement by argon; the slurry was then allowed to settle and samples of supernatant liquid removed for analysis. As has been observed by other workers, it was found that on reintroduction of monomer polymerization continued as if it had not been interrupted. Advantage was taken of this fact to study the effects of changes in activator solution, which could be removed by decanting from the solid and washing with fresh diluent while under argon. No loss in activity occurred provided air and moisture were rigidly excluded. Monomer was then reintroduced with or without fresh activator.

Catalyst and activator were destroyed by addition of *n*-butanol, and Ti and Al removed by washing with water in an inert atmosphere. The supernatant liquid was then sampled to determine the proportion of soluble polymer formed which was weighed after evaporation of the sample. Samples of insoluble polymer for intrinsic viscosity determination were isolated by decanting diluent at polymerization temperature, followed by washing with cold heptane and acetone, and by drying *in vacuo*.

Labeling of polymer molecules was carried out by addition to the polymer slurry under argon of a xylene solution of iodine in excess of all metal-alkyl groups present. After half an hour *n*-butanol was added and excess iodine, aluminum, and titanium compounds and soluble polymer were removed as for intrinsic viscosity samples. The percentage of iodine still left in the polymer was determined by complete combustion in oxygen, conversion of iodide to iodate, addition of excess iodide, and titration with thiosulfate. In this way 0.02 wt.-% iodine could be detected. A blank experiment wherein iodine was added immediately after the butanol showed no trace of iodine in the polymer.

Raw Materials

Monomer. Monomer was of greater than 99% purity, and especially low in impurities known to attack catalyst and alkyl, such as water (<50 ppm) and oxygen (<10 ppm).

Aluminum Alkyls. Aluminum alkyls were handled as 25% solutions in diluent and stored under nitrogen. These were periodically checked by analysis by using methods described below.

Catalysts. Various forms of violet $TiCl_3$ were prepared and characterized by chemical and x-ray analyses, results for the latter being compared with those which Natta has previously reported.[4] Hydrogen-reduced and aluminum-reduced $TiCl_4$ as supplied by Stauffer Chemicals Inc. were also tested. These catalysts were ground in a 5 in. diameter mill with stainless-steel balls in an inert atmosphere. Alkyl reduction of $TiCl_4$ was carried out under conditions yielding violet $TiCl_3$ complexes. On analysis titanium was shown to be almost entirely present in the trivalent state, consisting of solid solutions of $AlCl_3$ in $TiCl_3$ plus some $EtAlCl_2$ strongly adsorbed, but not involved in the crystal structure. The x-ray spectra resemble closely Natta's δ-$TiCl_3$.[4]

Analyses

Metalethyl groups were determined by hydrolysis and measurement of ethane evolved. Aluminum in absence of titanium was estimated by standard methods by using ethylenediaminetetraacetic acid. Chloride could be found by titration with NaOH and HCl or more accurately by electrometric titration with $AgNO_3$. For the dilute solutions of activator removed from polymerizations it was necessary to complete analysis within 24 hr. due to slow loss of Al^{+++} by hydrolysis and adsorption on glass. Traces of titanium in diluent were estimated colorimetrically after oxidation of a dilute acid extract with hydrogen peroxide. Trivalent titanium in catalysts was determined by titration with ceric sulfate.

RESULTS

Kinetics Studies

Polymerizations with these catalysts are characterized by induction periods of varying length depending on the catalyst type, during which breakup of particles occurs exposing the catalytic surfaces to the full. Rapid polymerization follows at rates proportional to the partial pressure of propylene and to the catalyst concentration. Conversion to polymer is measured conveniently as moles of monomer introduced after saturation of diluent per mole of $TiCl_3$, and polymerization rates expressed as conversion per hour per atmosphere. In all cases where Et_2AlCl is used as activator a slow loss of activity occurs as polymerization proceeds. An understanding of these changes has been achieved by studying the effects of renewing the activator solution by the technique described in the experimental section and by studying the inhibition of polymerization by added $EtAlCl_2$, which was suspected to be a by-product derived from the activator. In all these experiments little change in the yield of insoluble polymer (about 97% of monomer polymerized) or its intrinsic viscosity at a given conversion was observed whether inhibitor was added or removed.

A feature common to all catalysts studied was that renewal of activator solution produced an increase in activity, which in some cases was appreci-

ably higher than the initial rate. After renewal, activity again declined slowly as propylene was polymerized. Catalysts prepared by aluminum alkyl reduction of $TiCl_4$ were distinguished in that the maximum rate, R_0, obtained in this manner was independent of the amount of monomer polymerized. The highest rates obtainable with aluminum-reduced $TiCl_4$ activated by ball-milling decreased as polymerization proceeded, indicating that in this case some permanent loss in activity was occurring besides that caused by changing activator composition. This particular aspect of rate loss was not studied further in the present work.

The quantitative relationship between inhibitor added [I] (moles $EtAlCl_2$ per liter) and rate R was deduced from a series of experiments on each catalyst, such as that illustrated in Figure 1.

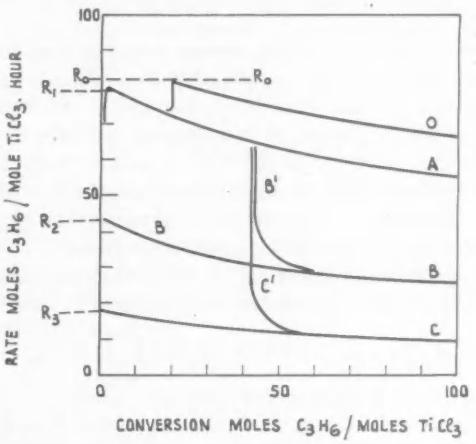

Fig. 1. Polymerization with varying compositions of activator solutions (50°C., 10 mmoles/l. of catalyst made by alkyl reduction of $TiCl_4$, 20 mmoles/l. Et_2AlCl): (O) activator removed at low conversion and fresh introduced; (A) standard conditions; (B, C) effect of adding 5 and 20 mmoles/l. $EtAlCl_2$ to initial activator solution; (B', C') effect of adding 5 and 20 mmoles/l. $EtAlCl_2$ after a conversion of 42 moles C_3H_6/mole $TiCl_3$.

In all these experiments a fall in rate with conversion is evident, and to estimate the effect of added $EtAlCl_2$ rates R_1, R_2, R_3, etc., from extrapolation to zero conversion were found. The relationship found between [I] and R can be expressed in terms of eq. (1)

$$(R^0 - R)/R = k([I] + [I]_0) \tag{1}$$

Under standard conditions the rate is prevented from reaching the maximum, R_0, by generation of inhibitor of strength equivalent to $[I_0]$ moles $EtAlCl_2$ per liter. Sensitivity of the catalyst to this inhibitor is measured by values of k, and loss of initial activity is given by $k[I_0]$. Results for a variety of catalysts are presented in Table I.

TABLE I
Effect of $EtAlCl_2$ Inhibition with Various Forms of $TiCl_3$[a]

Catalysts				
Reagent for $TiCl_4$ reduction	Mole ratio of cocrystallized $AlCl_3/TiCl_3$	k, l./mmole	$[I_0]$, mmole/l.	R/R_0
Hydrogen	0	0.4	<0.5	>0.96
Al alkyl	0.15	0.17	0.6	0.91
Al metal	0.33	0.27	1.7	0.69
Al alkyl	0.4	0.22	2.5	0.65
Al alkyl	1.0	0.13	4.0	0.66

[a] Polymerizations were carried out at 50°C. with 20 mmole/l. activator and 10 mmole/l. catalyst.

The extent of initial reaction with activator as measured by $[I_0]$ in Table I varies directly with $AlCl_3$ cocrystallized with $TiCl_3$, whereas values of k with one exception increase with decreasing $AlCl_3$. If catalysts are pretreated with activator before polymerization, washed free of soluble reaction products, and fresh activator added with monomer, polymerization proceeds with $[I_0]$ reduced to undetectable level; values of k, however, are little altered by this procedure. A discussion of these facts is given in the next section on reaction of activator during polymerization.

Some indication as to the nature of the inhibiting species can be deduced from eq. (1), which may be rewritten in the form

$$R/R_0 = 1/\{1 + k([I] + [I_0])\} = (1 - \theta) \tag{2}$$

which resembles a simple Langmuir isotherm, where θ is the fraction of catalyst surface covered by reversible adsorption of inhibiting species. The rate of adsorption of the latter is proportional to the concentration of ethylaluminum dichloride in solution which is known to exist in dimeric form involving chloride bridge structure.[10,11] Rapid interchange of substituents is known to occur, and concentrations of species present are presumably controlled by equilibria such as eq. (3)

$$Et_4Al_2Cl_2 + Et_2Al_2Cl_4 \rightleftharpoons 2\ Et_3Al_2Cl_3 \tag{3}$$

In the presence of excess activator most of the added inhibitor is present as $Et_3Al_2Cl_3$. If this is the species actually adsorbed, eq. (1) becomes

$$(R_0 - R)/R = k([I_0] + [Et_3Al_2Cl_3]) \tag{4}$$

Alternatively, monomeric $EtAlCl_2$ may be the only entity small enough to be adsorbed on the catalyst. Concentrations of this species are governed by slight dissociation of alkyls present

$$Et_3Al_2Cl_3 \rightleftharpoons Et_2AlCl + EtAlCl_2$$

$$Et_4Al_2Cl_2 \rightleftharpoons 2\ Et_2AlCl$$

Hence the concentration of $EtAlCl_2$ is given by

$$\begin{aligned}[EtAlCl_2] &= k_c[Et_3Al_2Cl_3]/[Et_2AlCl] \\ &= k_c[Et_3Al_2Cl_3]/(k_d[Et_4Al_2Cl_2])^{1/2} \\ &\simeq K[I]/[A]^{1/2}\end{aligned}$$

where k_ck_d, and K are constants, [I] is the concentration of inhibitor and [A] the concentration of activator present.

Equation (1) then becomes

$$(R_0 - R)/R = k\,([I] + [I_0]) = k'([I] + [I_0])/[A]^{1/2} \qquad (5)$$

In practice k was found to vary inversely as the square root of activator concentration; this supports eq. (5) rather than eq. (4), and thus provides evidence that monomeric $EtAlCl_2$ is the inhibiting species.

A variety of compounds can remove $EtAlCl_2$ without having much effect on Et_2AlCl. For example, NaCl can increase polymerization rate temporarily to the maximum, R_0, due to removal of $EtAlCl_2$ as an insoluble complex:

$$NaCl + EtAlCl_2 \rightarrow Na(EtAlCl_3)$$

In this case continued reaction is prevented by NaCl becoming protected by a coating of complex. Better results are obtained by using complex salts such as $K(Et_2AlCl_2)$, which can be finely dispersed in the paraffin diluent by addition as a concentrated solution in xylene.[12] $K(Et_2AlCl_2)$ has the advantage of generating one molecule of fresh activator for every molecule of inhibitor removed

$$K(Et_2AlCl_2) + EtAlCl_2 \rightarrow Et_2AlCl + K(EtAlCl_3)$$

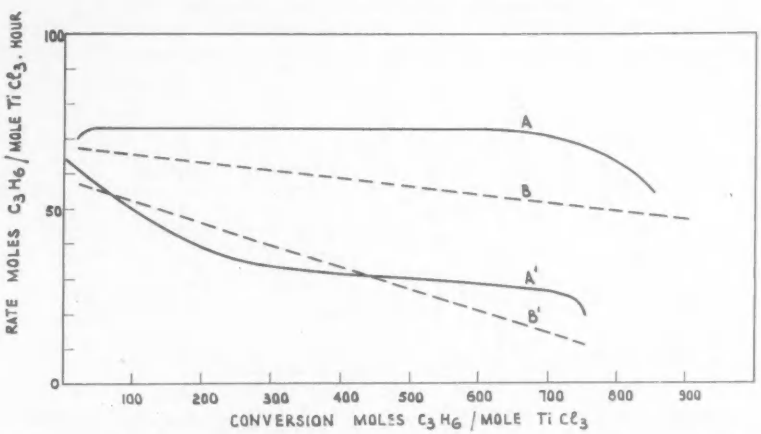

Fig. 2. Effects of complexing agents on the polymerization of propylene (50°C., 10 mmoles/l. of catalyst, 20 mmoles/l. of activator): (A) alkyl aluminum-reduced $TiCl_4$; (B) aluminum metal-reduced $TiCl_4$ in the presence of complexing agent; (A') and (B') the same catalysts, respectively, in absence of complexing agent.

With this complexing agent the equivalent of repeated decanting and renewal of activator can be reproduced; this is illustrated for two catalysts in Figure 2.

With alkyl-reduced $TiCl_4$ activity can be maintained at the maximum R_0. In the case of aluminum-reduced $TiCl_4$, a considerable improvement is effected, but the polymerization rate R_0 decreases slowly with conversion, just as is found in the activator renewal experiment.

Controlled addition of Et_3Al can also be used to maintain maximum rate, when inhibitor is removed by the reaction

$$Et_3Al + EtAlCl_2 \rightarrow 2EtAlCl$$

It is, however, difficult to avoid addition of excess Et_3Al which appears to reduce the catalyst (the color changes from violet to black) with accompanying rapid increase in rate and marked loss of stereospecificity.

Increased activity observed on addition of minor amounts of other salts, ethers, amines, etc.[13] is also explicable in terms of removal of inhibitor,[11] if it is assumed that the preferred order of stability of complexes is $EtAlCl_2 > Et_2AlCl$. Thus, the addition of 5 mmoles/l. of hexamethylphosphoramide to a polymerization with 10 mmoles/l. of catalyst and 20 mmoles/l. of activator was found sufficient to raise the polymerization rate to the maximum.

Catalysts may be activated with $EtAlCl_2$ to produce high polymers in the presence of complexing agents;[14] in this case the equilibrium

$$Et_2Al_2Cl_4 \rightleftharpoons Et_2AlCl + AlCl_3$$

is displaced to the right by preferred reaction with $AlCl_3$.

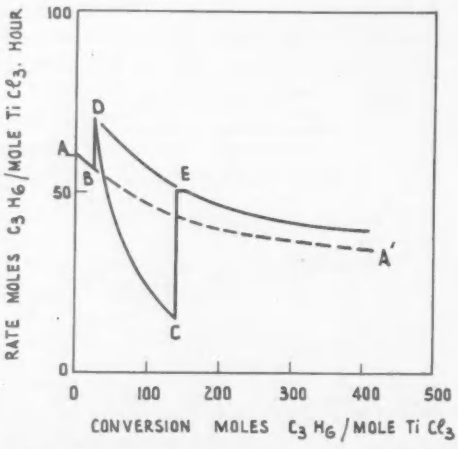

Fig. 3. Polymerization in absence of activator: (*A–A*) standard run; (*B*) activator removed at low conversion and replaced by diluent only; (*D–C*) polymerization in absence of activator; (*C*) fresh activator introduced; (*D–E*) activator removed as for *B*, and fresh activator reintroduced with diluent.

A further important feature of polymerizations with $TiCl_3$ is that the presence of activator is necessary to sustain reaction for long periods. Stereospecific polymerization can take place for a short time at high rate without Et_2AlCl in solution provided either that the catalyst has been pretreated with activator and washed or a normal polymerization is interrupted and activator replaced by diluent only. Such an experiment is illustrated in Figure 3 by the relatively rapid rate loss (B to C) in absence of activator which can be recovered by addition of fresh activator.

From the kinetics study the threefold character of the activator has been demonstrated: initiation of reaction, production of inhibitor, and sustaining of polymerization, which are connected by reactions deduced from analysis described in the next section.

Reaction of Activator during Polymerization

Samples of activator solution were removed from polymerizations by the methods described in the experimental section, and analyzed for aluminum, chlorine, and ethyl groups hydrolyzable to ethane, i.e., present as ethylaluminum compounds. Small amounts ($<1/2$ mg.-atom/l.) of titanium were also found. During polymerization chlorine concentration remained constant, whereas at the early stages a marked loss from solution of aluminum and ethyl in the ratio 1:3 occurred. Thus the activator behaves as if it disproportionates, leaving in solution one equivalent of inhibitor and transfering to solid the equivalent of triethylaluminum

$$Et_4Al_2Cl_2 \rightarrow \underset{\text{(absorbed by solid)}}{Et_3Al} + \underset{\text{(left in solution)}}{EtAlCl_2} \qquad (6)$$

As seen from Table II the quantities of inhibitor measured by analysis agree well with values for $[I_0]$ deduced from inhibitor studies described in the section on kinetics [eq. (1)].

TABLE II
Reaction of Activator at Early Stages of Polymerization

Catalyst reagent for reduction of $TiCl_4$	Polymerization temperature, °C.	Initial inhibitor concn., $[I_0]$, mmoles/l.	Loss of Et_3Al, mmoles/l.
Aluminum metal	50	1.7	1.4–1.9
Aluminum alkyl	50	2.5	2.5
Aluminum alkyl	60	1.5	1.05

Having demonstrated the initial reaction with activator, it was necessary to show how much of this is actually involved in forming active centers. The chemical nature of these centers is unknown, but the overall polymerization reaction is probably the same as that deduced by Natta for α-$TiCl_3$ activated by Et_3Al and Et_2AlCl.[18] Natta showed that an ethyl

group from the activator becomes attached to each polymer chain at the end remote from the catalysts:

$$[\text{Cat}]\text{—Et} + C_3H_6 \rightarrow [\text{Cat}]\text{—}CH_2\overset{\overset{CH_3}{|}}{C}H\text{—Et} \xrightarrow{C_3H_6} [\text{Cat}]\text{—}(CH_2\overset{\overset{CH_3}{|}}{C}H)_2\text{—Et} \qquad (7)$$

At early stages of polymerization, before appreciable rate loss occurs, it may be assumed that each active center is responsible for the loss of one ethyl group according to eq. (7). The rest of the ethyl groups in solution and solid are present as organometallic compounds and so can be hydrolyzed by dilute sulfuric acid with production of ethane. Analysis showed that most of the initial reaction with activator, the extent of which is given in Table II, was not involved in polymerization, since ethyl groups not accounted for by hydrolysis amounted to less than 0.01 moles/mole $TiCl_3$.

The initial reaction of activator according to eq. (6) as measured by $[I_0]$ is proportional to the $AlCl_3$ content of the catalyst, as pointed out in the previous section. It is well known that free $AlCl_3$ dissolves rapidly in diethylaluminum chloride to form $EtAlCl_2$. This is considerably reduced if $AlCl_3$ is cocrystallized with $TiCl_3$, when the main reaction in absence of monomer is a partial exchange of chloride with ethyl radicals from solution, presumably limited to such $AlCl_3$ groups as are situated round the edges of crystallite regions:

$$[TiCl_3]_nAlCl_3 + aEt_2AlCl \rightarrow [TiCl_3]_n(Et_aAlCl_{3-a}) + aEtAlCl_2 \qquad (8)$$

If eq. (8) is also the first step occurring in presence of monomer, $aEtAlCl_2$ is the initial inhibitor produced, $[I_0]$. Hence pretreatment of the catalyst with activator in absence of monomer followed by washing, markedly reduces $[I_0]$, as is observed in practice. Normally reaction (8) must be followed by adsorption of the equivalent number of Et_2AlCl molecules at Al—Et bonds exposed on the catalyst surface, thus restoring the chloride concentration in solution to that of the initial activator.

$$[\text{Cat}]\rangle\text{Al—Et} + Et_2AlCl \rightarrow [\text{Cat}]\rangle\text{Al}\overset{\overset{Et}{|}}{\underset{\underset{Et}{|}}{}}\text{Al}\overset{\overset{Et}{|}}{\underset{\underset{Cl}{|}}{}} \qquad (9)$$

The net result of reactions (8) and (9) is then equal to eq. (6). To account for such extensive reactions with edge $AlCl_3$ groups, crystallite sizes must be very small (about 50–100 A.), for which there is some evidence from the diffuseness of some lines in the x-ray spectrum. The reasons for preference of ethyl bridges at the surface is unknown, although these have been postulated for alkylaluminum chlorides as existing in solution in tautomeric equilibrium with chloride bridges.[11b] The reaction of surface $TiCl_3$ groups is considerably weaker as judged by adsorption of Et_3Al and Et_2AlCl on α-$TiCl_3$,[1a] and so the corresponding contributions to $[I_0]$ are expected to be much less. This is supported by the fact that $[I_0]$ found for α-$TiCl_3$ (Table I) was too small to be measured.

The nature of the reactions initiating polymerization is obscured by changes caused by the presence of $AlCl_3$. The ethyl–catalyst bonds taking part in reactions such as eq. (7) must be part of the general formation of metal–ethyl bonds on the catalyst surface, and presumably owe their special activity to being located on Ti atoms or in aluminum–titanium alkyl complexes. Inhibition by $EtAlCl_2$ may be considered as a reverse of the above process substituting chloride for ethyl. In view of the rarity of centers active in polymerization the concentration of $EtAlCl_2$ in solution is little affected by this inhibiting reaction.

After the initial loss activator is consumed much more slowly, as seen from Figure 4 for polymerization at 60°C. with alkylaluminum–reduced $TiCl_4$ as catalysts.

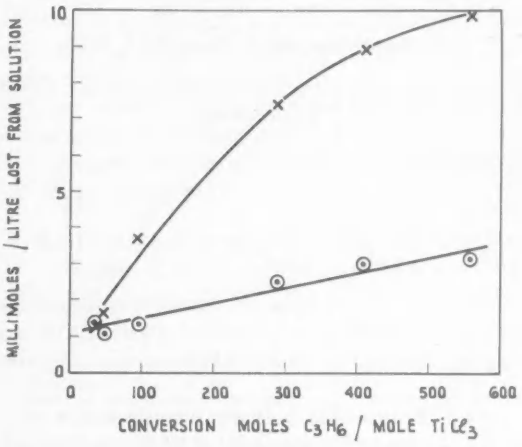

Fig. 4. Analysis of alkyl in diluent (60°C., 10 mmoles/l. catalyst, 20 mmoles/l. Et_2AlCl): (⊙) Aluminum; (×) 1/3 organo-metallic ethyl groups.

Due to continued loss of aluminum from solution without change in chloride concentration, the concentration of alkylaluminum dichloride inhibitor correspondingly increases as polymerization proceeds. The polymerization rate curve can be predicted from aluminum analyses combined with a knowledge of R_0 and k from inhibitor studies [eq. (1)]. Reasonable agreement is found between calculated and observed rate curves, as shown in Figure 5.

Loss of aluminum into the solid polymer is explicable if the observations of a number of workers[1–3] that some polymer molecules retain alkylaluminum endgroups are taken into account. In the systems being studied these can arise from chain-transfer reactions where polymer with diethylaluminum endgroups become detached from the catalyst surface, which is then reactivated by fresh Et_2AlCl.

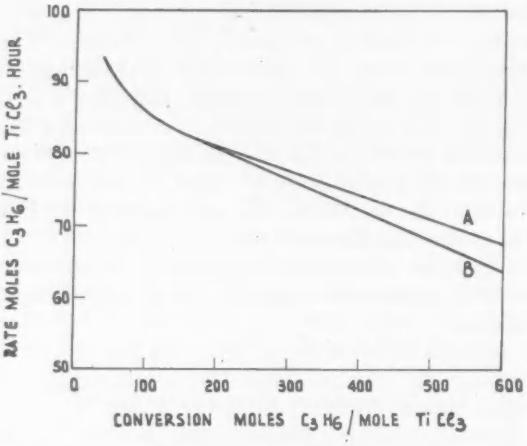

Fig. 5. Comparison of observed and calculated rate curves: (*A*) observed; (*B*) calculated.

The net reaction is

$$\underset{\text{solid}}{[\text{Cat}]\text{—}(CH_2\underset{|}{\overset{CH_3}{C}}H)_n\text{Et}} + \underset{\text{solution}}{2\ Et_2AlCl} \rightarrow \underset{\text{solid}}{[\text{Cat}]\text{—Et}} + \underset{\text{solid}}{Et_2Al(CH_2\underset{|}{\overset{CH_3}{C}}H)_n\text{Et}} + \underset{\text{solution}}{EtAlCl_2} \quad (10)$$

The fact that chloride concentration in solution remains constant indicates that ethyl–chloride exchange is not possible between $EtAlCl_2$ and polymer alkyl. Presumably the latter is protected by inclusion in growing polymer crystallites.

Equation (10) indicates that polymer chain transfer with aluminum alkyl results in a net loss of the elements of Et_3Al from the solution to the solid. In Figure 4 it is seen that the loss of hydrolyzable ethyl groups from solution exceeds the amount required to balance the aluminum loss; it is believed that this is due to the soluble polymer (6% of the total polymer in this experiment including oils) also being largely terminated by —$AlEt_2$, so that the excess loss of hydrolyzable ethyl groups is balanced by a gain of polymeric alkyl groups in solution.

The ability to attach various endgroups, such as iodine, to polymer molecules by reactions which are well established for aluminum alkyls of low molecular weight is a proof of the presence of organometallic endgroups, and affords a method for studying the relationship between molecular weight and consumption of activator, described in the next section.

Molecular Weight Studies

Fractionation experiments in these laboratories have confirmed the general view that molecular weight distributions of polymers from catalysts of this type are broad, which has been ascribed to variations in the ratio of

propagation to transfer rates at different parts of the catalyst surface. A viscosity-average molecular weight, $\bar{M}_v$, derived from the Kinsinger-Hughes relation[15] has been found to approximate to a weight-average molecular weight. To relate activator changes to formation of polymer molecules a number-average, $\bar{M}_n$, is essential. Hence the technique of Chien involving use of iodine to label polymers has been employed with differences in the methods of analysis. Here it is assumed that one iodine atom becomes attached to the end of each polymer molecule which is terminated by an aluminum alkyl group. Polymers not containing such endgroups will escape labeling, and so values of $\bar{M}_n$ derived may be high. The ratio $\bar{M}_v/\bar{M}_n$ is a measure of the broadness of molecular weight distribution. Although it is not known how the latter varies throughout a given polymerization, the ratio may be compared to values of 5–7 obtained from fractionation experiments on polymer of high conversion. Assuming little change in distribution occurs during polymerization, the ratio may be used as a rough check on $\bar{M}_n$.

In Table III are reported results from the same polymerization at 60°C. discussed above which was used for activator studies (see also Figs. 4 and 5), so that a direct comparison can be made between molecular weight growth and consumption of activator.

TABLE III
Iodine Labeling of Polymer Made at 60°C.

Conversion, moles C_3H_6/ mole $TiCl_3$	Iodine, wt.-%	Calculated $\bar{M}_n \times 10^{-3}$	$\bar{M}_v \times 10^{-3}$	$(\bar{M}_v/\bar{M}_n)$	Polymer, moles/mole of $TiCl_3$ $\times 10^3$
15.5	0.18	70	—	—	9
35	0.11	115	410→	3.6	13
48	0.08	160	460	2.9	12
96	0.08	160	540	3.4	26
289	0.07	180	800	4.4	68
410	0.06	210	880	4.2	82
557	0.05	250	1000	4.0	94

The quantity in the sixth column of Table III is derived by dividing the conversion (moles of monomer polymerized per mole of $TiCl_3$) by the degree of polymerization (average number of moles of monomer per mole of polymer). As seen from Figure 6 this quantity increases throughout, and up to 300 moles C_3H_6/mole $TiCl_3$ the increase is linear with respect to conversion.

Over the linear portion of Figure 6 the polymerization rate dropped from 75 to 65% of the maximum rate attainable with this catalyst by renewing the activator, and so to a first approximation the moles of active centers per mole $TiCl_3$, C^*, which have not been affected by inhibitor, may be assumed to be constant. Assuming also that the number of polymer

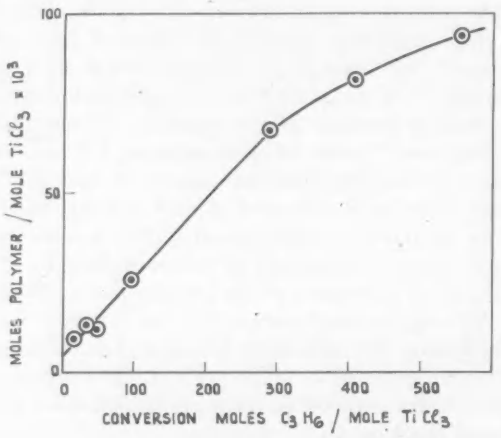

Fig. 6. Variation in moles of polymer produced per mole of catalyst with conversion.

molecules per mole $TiCl_3$ which have undergone a transfer reaction and are no longer growing is proportional to the conversion Q, the total polymer labeled by iodine, n, is then given by

$$n = C^* + k_{tr}Q$$

Values of the constants C^* and k_{tr} can be deduced from Figure 6. The intercept in Figure 6 gives a low figure of 4×10^{-3} moles active centers per mole $TiCl_3$; this is in agreement with the observation from analytical data for the initial reaction with activator, described in the previous section, that less than 0.01 moles of metal-ethyl groups per mole of $TiCl_3$ can be involved in initiating polymerization. The rate of the transfer reaction, R_{tr} moles polymer transferred per mole $TiCl_3$ per hour is given by

$$R_{tr} = R_p k_{tr}$$

where R_p is the mean polymerization rate. From this it is calculated that on average 5 polymers are grown on each active center per hour, that is, a mean growth time of about 12 min.

The molecular weight is related to n by the equation

$$\bar{M}_n = 42\ Q/n$$

which has been used in conjunction with values of C^* and k_{tr} to compare calculated $\bar{M}_n$ with the observed value (Fig. 7). After 300 moles C_3H_6/mole $TiCl_3$ a steady rise in $\bar{M}_n$ occurs which is probably connected with the changing chemical nature (loss of ethyl groups) of the activator solution.

The ratios $\bar{M}_v/\bar{M}_n$ in Table III are a little lower than expected; values of $\bar{M}_n$ may be too high due to incomplete reaction with iodine, since it has been reported that it is difficult to get the third alkyl group on aluminum to react.[11c] Alternatively, other transfer reactions may be occurring, dis-

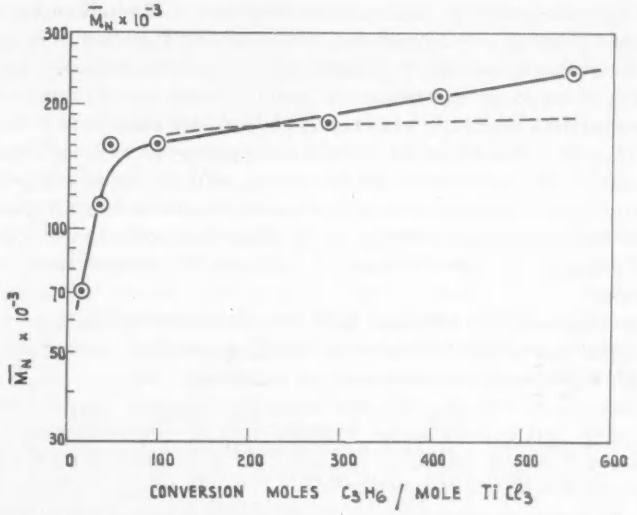

Fig. 7. Increase in molecular weight with polymerization at 60°C.: (⊙) observed; (- -) calculated.

cussed below, which do not leave aluminum attached to polymer. However, the reactions described above may be taken to apply at least to a large proportion of the polymer.

A consequence of the proposed reaction scheme is that aluminum involved in transfer reactions is related to that lost from solution as measured analytically, apart from the initial nonactivating reaction with catalyst. These quantities should be equal if only one high polymer molecule is attached to each aluminum. Over the range 100–300 moles C_3H_6 polymerized per mole $TiCl_3$, before molecular weights deviate from those calculated, 0.05 ± 0.02 g.-atoms Al/mole $TiCl_3$ were found attached to polymer by iodine labeling whereas 0.08 ± 0.03 g.-atoms/mole were lost by the solution. Within the fairly wide limits of error, these measurements provide extra evidence supporting the reaction mechanism proposed connecting molecular weight with consumption of activator.

DISCUSSION

The thesis of this paper is the relationship between the behavior of activator and the production of polypropylene as polymer aluminum alkyl. As a working model it was assumed that $TiCl_3$ behaves as a true catalyst capable of developing a number of active centers which remains constant throughout polymerization apart from those inhibited by monomeric $EtAlCl_2$ generated as by-product from the activator. It has been demonstrated that $EtAlCl_2$ is adsorbed reversibly on the catalyst with little effect

on the stereospecificity of the polymerization or the molecular weight (intrinsic viscosity) of the polymer, thus enabling the kinetics of the systems to be studied in spite of changing rates of polymerization. The main reaction of activator in presence of monomer was seen to involve a disproportionation whereby the elements of Et_3Al are absorbed by the solid, which is responsible for (*a*) an initial nonactivating reaction with cocrystallized $AlCl_3$, (*b*) formation of active centers, and (*c*) sustaining polymerization activity. The production of polypropylene aluminum alkyl has been related to the continual consumption of Et_3Al from activator, which on the model adopted has been interpreted in terms of a chain-transfer process with alkyl.

Four chain-transfer processes have been described by Natta.[1]

A. Spontaneous decomposition of growing polymer, leaving a catalyst hydride which is slowly reactivated by monomer:

$$[Cat]—(CH_2—\underset{|}{\overset{CH_3}{C}}H)_nEt \rightarrow [Cat]—H + CH_2=\underset{|}{\overset{CH_3}{C}}—(CH_2—\underset{|}{\overset{CH_3}{C}}H)_{n-1}Et$$

$$[Cat]—H + C_3H_6 \rightarrow [Cat]—C_3H_7$$

B. Transfer involving monomer; the rate is proportional to propylene pressure:

$$[Cat]—(CH_2—\underset{|}{\overset{CH_3}{C}}H)_nEt + C_3H_6 \rightarrow [Cat]—C_3H_7 + CH_2=\underset{|}{\overset{CH_3}{C}}—(CH_2—\underset{|}{\overset{CH_3}{C}}H)Et$$

C. Direct transfer with aluminum alkyl in solution; the rate of this reaction depends on the concentration of monomeric Et_3Al in solution and is independent of pressure:

$$[Cat]—(CH_2—\underset{|}{\overset{CH_3}{C}}H)_nEt + Et_3Al \rightarrow [Cat]—Et + Et_2Al(CH_2—\underset{|}{\overset{CH_3}{C}}H)_nEt$$

D. Transfer with aluminum alkyl in solution dependent on the concentration of $TiCl_3$ and on propylene pressure. The reaction is formally the same as reaction C, but to explain the dependence on $TiCl_3$ it is proposed that the transfer is catalyzed by a soluble product derived from $TiCl_3$.

Reaction A is not considered to be important below about 80°C. Evidence that reaction B is of minor importance with $TiCl_3$ catalysts activated by Et_2AlCl is derived from the fact that in the present work double bonds could not be detected by infrared spectroscopy, i.e., the concentrations of double bonds is less than one per 7000 monomer units. This is even true for polymer made at 90°C. for which a mean degree of polymerization of about 1000 was deduced by ebulliometry and iodine labeling.

The transfer reaction most applicable to the present work must lead to the correct relationship between molecular weight and pressure. We have observed that molecular weight is independent of pressure over a range of 1–7 atm. when comparison is made at a fixed conversion. The apparently contradictory results of Bier[5] are in fact in agreement, if again a fixed conversion is taken instead of the polymerizations quoted carried out for

fixed times. The molecular weight is determined by the ratio of propagation to transfer rates, and, since the former is proportional to pressure of monomer, so must be the rates of transfer. This rules out reaction C, which is also unlikely, since the Et_3Al concentration will be very low using Et_2AlCl as activator. Reaction D has the dependence on pressure required. The presence of titanium in solution has been detected in the present work in systems using Et_2AlCl, but it is not known how this affects the molecular weight. Reaction D closely resembles eq. (10) proposed as the main transfer reaction occurring in the present systems. The dependence of reaction (10) on pressure of monomer can be explained, if the transfer reaction is considered as a relatively rare deviation from the normal propagation process, i.e., the chances of it occurring are related directly to the number of monomer units being added. The faster these are added (higher C_3H_6 pressures), the more chance transfers will occur. Natta has proposed that the propagation process and this type of transfer share the same activated state. Catalyst–polymer bonds are weakest during the addition of a monomer unit. If activation energy is concentrated at the right moment into these bonds (a relatively rare possibility) complete detachment of polymer aluminum alkyl from the catalyst occurs before the addition of the next monomer is completed.

The short times of growth of about 12 min. deduced from the adopted working model are apparently at variance with the findings of Kontos[9] and Bier,[6] based on the observation that removal of monomer for periods of 15 hr. does not affect plots of polymerization rates or polymer reduced solution viscosity against conversion. These times of interruption are not necessarily, however, a measure of the growth time during polymerization. On the mechanism of the transfer reactions proposed above it is seen that removal of monomer suspends both propagation and transfer, since no activation of polymer–catalyst bonds can occur.

The results of Kohn et al.,[7] who used aluminum-reduced $TiCl_4$ as catalyst, may be interpreted in terms of the present working model, but complications arise in the one example fully described (Run A) at high conversions due to the extremely large rate changes (more than a 10-fold drop) and to the relatively low quantities of activator used. Taking molecular weights from tritium labeling a reasonable fit for the molecular weight curve up to 1.5 hr. polymerization can be obtained assuming 8×10^{-3} active centers per mole $TiCl_3$ and an initial growth period of about 15 min. From experience with similar systems at I.C.I. the loss of rate with polymerization can largely be accounted for by accumulation of inhibitor and exhaustion of activator.

The present paper has been concerned with a proper understanding of the behavior of diethylaluminum chloride as activator with various types of $TiCl_3$ catalysts. This has provided a key to the solution of many problems involved, including the production of active centers and the control of molecular weight. An explanation has been offered for the effect of certain additives in increasing the activity without loss of stereoregularity. The

behavior of various important catalysts including those formed with $AlCl_3$ cocrystallized with $TiCl_3$ has been related to one simple working model.

ADDENDUM

Since the above paper was submitted two publications have appeared, and were commented on at the Symposium. J. C. W. Chien [*J. Polymer Sci.*, **A1**, 425 (1963)] studied polymerizations with α-$TiCl_3$ activated by Et_2AlCl. As in the present work he interpreted the observed growth in molecular weight with conversion by chain transfer reactions involving consumption of alkyl, but the particular course of these reactions could not be deduced as no complete analyses of alkyl solutions were made during polymerization. Indeed with these particular catalysts at 50°C. it would be very difficult to achieve sufficient accuracy as very little inhibitor was being produced and reaction rates were constant within experimental error. The latter is consonant with the very long growth times of polymer chains which can be calculated from Chien's data using the method outlined in the above paper.

G. Bier et al. [*Makromol. Chem.*, **58**, 1 (1963)] have compared α-$TiCl_3$ activated with Et_3Al, a system studied extensively by Natta, with $TiCl_3$ prepared by aluminum alkyl reduction of $TiCl_4$ activated by Et_2AlCl. Bier assumed, as in earlier publications cited above, that transfer reactions are of no importance in the latter system, and was forced to make the unlikely assumption that the number of active centers increases rapidly over the first hour of reaction whereas the observed activity actually decreases.

We have taken Bier's experimental results set forth in Table 2 (page 6) and plotted the variation in moles of polymer produced per mole of catalyst against conversion as described in the above paper. Apart from two final erratic points these data are in excellent agreement with the working model described in the present work which also affords a simpler explanation of activity loss which has been checked by experiment. For Bier's two catalysts produced by alkyl reduction of $TiCl_4$ we find polymer growth times at 50°C. of 30 min. and 1.2 hr., i.e., somewhat longer than the example we have quoted at 60°C.

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Synopsis

Polymerization of propylene has been studied using as catalysts titanium trichloride complexed with varying amounts of aluminum compounds. A high degree of stereospecificity and activity can be sustained in the presence of $AlEt_2Cl$. Reaction of these catalysts with $AlEt_2Cl$ follows a different course in the presence and absence of monomer. It is shown that in the former case an inhibitor, $AlEtCl_2$, is produced in solution by disproportionation of $AlEt_2Cl$; the $AlEt_3$ concurrently produced is absorbed into the catalyst to form the activated species. The inhibitor can be removed by filtration, controlled reaction with $AlEt_3$, or complexing with a wide variety of organic or inorganic compounds. During the polymerization further $AlEt_2Cl$ is consumed; this is best interpreted in terms of Natta's chain-transfer mechanism with aluminum alkyl. It is found that even on polymerization at 90°C. the isotactic polypropylene produced has no detectable terminal unsaturation, confirming that this transfer mechanism predominates.

Résumé

La polymérisation du propylène a été étudiée en employant comme catalyseurs le trichlorure de titane complexé avec différentes quantités de composés d'aluminium. Un degré élevé de stéréospécificité et d'activité peut être obtenu en présence de $AlEt_2Cl$. La réaction de ces catalyseurs avec $AlEt_2Cl$ progresse d'une façon différente en présence et en absence de monomère. On montre que dans le premier cas un inhibiteur, $AlEtCl_2$ est produit en solution par disproportionnement d'$AlEt_2Cl$; le $AlEt_3$, produit concurrammment, est absorbé par le catalyseur pour former l'espèce activée. L'inhibiteur peut être en levé par filtration et on peut contrôler la réaction avec $AlEt_3$ ou former un complexe avec une grande variété de composés organiques ou inorganiques. Pendant la polymérisation ultérieure $AlEt_2Cl$ est consommé; la meilleure explication est de faire appel au mécanisme de transfert de chaîne de Natta avec l'aluminium alcoyle. On montre que même par polymérisation à 90°C, le polypropylène isotactique formé ne présente pas d'insaturation terminale détectable, ce qui confirme que ce mécanisme de transfert est prédominant.

Zusammenfassung

Die Polymerisation von Propylen mit Komplexen aus Titantrichlorid und verschiedenen Mengen von Aluminiumverbindungen als Katalysator wurde untersucht. Hohe Stereospecifität und Aktivität kann in Gegenwart von $AlEt_2Cl$ erhalten werden. Die Reaktion dieser Katalysatoren mit $AlEt_2Cl$ nimmt in Gegenwart und Abwesenheit des Monomeren einen verschiedenartigen Verlauf. Es wird gezeigt, dass im ersteren Falle durch Disproportionierung von $AlEt_2Cl$ in Lösung ein Inhibitor, $AlEtCl_2$, gebildet wird; das gleichzeitig entstehende $AlEt_3$ wird vom Katalysator unter Bildung der aktivierten Form absorbiert. Der Inhibitor kann durch Filtration, kontrollierte Reaktion mit $AlEt_3$ oder Komplexbildung mit einer grossen Zahl organischer oder anorganischer Verbindungen entfernt werden. Während der Polymerisation wird weiteres $AlEt_2Cl$ verbraucht; das lässt sich am besten auf Grund des Kettenübertragungsmechanismus mit Aluminiumalkyl von Natta verstehen. Sogar das bei einer Polymerisationstemperatur

von 90°C gebildete isotaktische Polypropylen besitzt innerhalb der Messgenauigkeit keine endständigen Doppelbindungen, was das Vorherrschen dieses Übertragungsmechanismus bestätigt.

Discussion

Dr. H. W. Coover (*Tennessee Eastman Co., Kingsport, Tenn.*): I should like to discuss a few points where our data disagree with those obtained in this investigation. In this paper, the increased activity observed on the addition of minor amounts of salts, ethers, amines, etc., was explained in terms of the removal of $EtAlCl_2$ through formation of a complex which was presumed to be more stable than a similar complex from Et_2AlCl. It was also stated that catalysts could be activated with $EtAlCl_2$ in the presence of complexing agents, but it was assumed that the $EtAlCl_2$ disproportionated to give Et_2AlCl and $AlCl_3$ and that the latter reacted with the complexing agent. While disproportionation reactions of alkylmetal halides are not uncommon, it should be noted that $EtAlCl_2$ forms stable complexes with the complexing agents in question, such as tertiary amines [F. M. Peters et al., *Can. J. Chem.*, **41**, 1051 (1963)]. In addition, we found that $EtAlCl_2$ and α-$TiCl_3$ in the presence of certain complexing agents, such as hexamethylphosphoric triamide, are active catalysts *per se*, and no Et_2AlCl was found to be present in these systems by infrared absorption analysis. The infrared spectrum of Et_2AlCl in benzene solution shows a characteristic absorption band at 18.3 μ. This band was absent in the infrared spectrum of benzene solutions of preheated mixtures of $EtAlCl_2$ and various complexing agents, and appeared in the spectrum of these mixtures only when Et_2AlCl had been added purposely. We further showed that the stereospecificity of the active site and the ability to resist chain transfer are different for sites formed with the three-component $EtAlCl_2$ catalysts and those formed with the two-component Et_2AlCl system.

The chain transfer reaction proposed by us,

$$Ti^*[X_2AlP] + EtAlX_2 + C_3H_6 \rightarrow Ti^*[X_2AlEt] + X_2Al\text{-}C_3H_6\text{-}P$$

where X can be alkyl or halogen, can explain the results observed in this paper. This reaction would explain why the monomer concentration does not influence the molecular weight of the polymer, why Et_2AlX is consumed during the polymerization, why no terminal unsaturation was detected, and why the rate falls off when the viscosity of the reaction mixture reduces the mobility of the Et_2AlX and, thereby, retards the regeneration of the active sites after transfer.

A. D. Caunt: In reply to the comments by Dr. H. W. Coover may I submit analytical data which demonstrate that Et_2AlCl can be produced in solution when $EtAlCl_2$ mM. of $EtAlCl_2$ in 120 ml. of a purified paraffin diluent were added to 108 mM. of $(C_4H_9)_4NI$[2]. After stirring for $5^1/_2$ hr. at room temperature the solid complex was separated and the solution analyzed. The latter was found to contain $49^1/_2$ mg. atoms of aluminum, 49 mg. atoms of chlorine, 93 mM. of ethyl hydrolyzable to ethane and 0.1 mg. atoms iodine. The solution thus contained about a quarter of the original aluminum which was now present as fairly pure Et_2AlCl. We propose that the following reactions had occurred:

$$EtAlCl_2 + (C_4H_9)_4NI \rightarrow (C_4H_9)_4N[EtAlCl_2I]$$

$$EtAlCl_2 + (C_4H_9)_4N[EtAlCl_2I] \begin{cases} \rightarrow (C_4H_9)_4N[EtAlCl_2I \cdot EtAlCl_2] \text{ (solid)} \\ \rightarrow Et_2AlCl \text{ (solution)} + (C_4H_9)_4N[AlCl_3I] \text{ (solid)} \end{cases}$$

Here the yield of Et_2AlCl is affected by a competing reaction to form a binary complex similar to those proposed by K. Ziegler et al. [*Ann.*, **629**, 33 (1960)]. We would emphasize that it is essential to have $EtAlCl_2$ in excess of the complexing compound pref-

erably in mole ratio of about 2:1.[2] Dr. Coover's reference to Peters et al. [*Can. J. Chem.* **41**, 1051 (1963)] is irrelevant to the point in dispute since in this case 1:1 complexes were prepared using excess of tertiary amines. Moreover, this work refers to replacement of chlorine in these complexes by hydrogen using $LiAlH_4$, and has no bearing on the ease with which alkyl complexes rearrange to generate Et_2AlCl. In the experiments of Dr. Coover where Et_2AlCl was not detected by infrared in solutions of $EtAlCl_2$ and complexing agents, we suggest that either too much complexing agent was present, or in these completely soluble systems the equilibrium concentration of Et_2AlCl was too low to be detected by such means. When equilibrium can be displaced, as by precipitation in the example we have quoted, formation of appreciable quantities of free Et_2AlCl can be easily demonstrated. It is suggested in our paper that such equilibria are similarly displaced during the formation of active centers in polymerization reactions and in chain transfer, which result in the removal of Et_2AlCl, or in the actual case studied, Et_3Al into the solid polymer. These changes can be properly studied only by analysis of activator solutions throughout the polymerization process.

Ample support for our own findings has been provided by the recently published work of Zambelli et al. [*J. Polymer Sci.*, **A1**, 403 (1963)] who have carried out similar analyses. Also in agreement with these authors we have found, in contrast to Dr. Coover, that the stereospecificity of polymerization, known to be sensitive to type of alkyl, is the same using $EtAlCl_2$ and a complexing agent as that from activation with Et_2AlCl alone.

Finally, the equation proposed by Dr. Coover for the transfer reaction,

$$Ti^*[X_2AlP] + EtAlX_2 + C_3H_6 \rightarrow Ti^*[X_2AlEt] + X_2Al - C_3H_6P$$

where X can be alkyl or halogen, cannot possibly be made to agree with the analytical facts of the present paper for Et_2AlCl activation. These facts are that the chlorine content of solution remains constant while the elements of Et_3Al are absorbed by the solid, and have led to a proposed transfer reaction (eq. 10) which is clearly not a particular case of Dr. Coover's equation. Fall-off in activity as polymerization proceeds has been equated in the paper quantitatively with the accumulation of the inhibitor, $EtAlCl_2$ which acts by reversible adsorption onto the catalyst. This fall-off cannot be due to growing polymer reducing the mobility of Et_2AlCl in replenishing active centers, as suggested by Dr. Coover. This is shown in experiments described in the paper wherein activity can be restored to more than the initial value by simply replacing the partially used activator containing $EtAlCl_2$ by fresh Et_2AlCl. Moreover, with finely divided catalysts a constant high activity can be maintained to high yields of conversions to polymer if the inhibitor is continuously removed by reaction with complexes such as $K[Et_2AlCl_2]$.

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Polymerization of Ethylene and Propylene with Ziegler-Natta Catalysts

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Although the number of publications is growing steadily quite a few problems in the heterogeneous polymerization with Ziegler-Natta catalysts are still open to discussion. The topic of this paper is a comparison of different catalytic systems in ethylene and propylene polymerization with respect to their behavior during the polymerization and to the viscosity of the products.

The catalytic system contained $TiCl_4$ or $TiCl_3$ (Stauffer AA) and various Al-organic compounds [$Al(C_2H_5)_3$, $Al(C_2H_5)_2Cl$, $Al_2(C_2H_5)_3Cl_3$, $Al(i\text{-}C_4H_9)_3$, $Al(i\text{-}C_4H_9)_2H$]. The course of the reaction was followed by measuring the monomer gas absorption from a buret. Variation of monomer concentration was obtained by addition of partial volumes of high purity dry N_2. Viscosity measurements were made in decalin at 135°C. at concentrations of 1 g./1000 ml.

A comparison of the different behavior of $TiCl_3$ and $TiCl_4$ in ethylene polymerization was made. With $TiCl_3$, by plotting monomer consumption vs. Al/Ti ratio we obtained adsorption isotherms contrary to findings of Natta[1] and Ambroz;[2] they are in agreement with the assumption that the AlR_3 (where R stands for $—C_2H_5$) compound is adsorbed on the surface of the catalyst while the monomer, however, seems to react directly from the solution (Fig. 1, curves *2* and *3*).

In this so-called Elay-Rideal mechanism the polymerization rate can be expressed by the eqs. (1) and (2):[3]

$$v = k\sigma_{Al}[M] \tag{1}$$

$$\sigma_{Al} = b_{Al}[Al]/(1 + b_{Al}[Al]) \tag{2}$$

where v is the rate of polymerizations, σ_{Al} is the fraction of surface covered by the Al compounds, [Al] and [M] are concentrations of AlR_3 and monomers; and k and b are constants.

Equations (1) and (2) can be transformed to

$$\frac{[Al]}{v} = \frac{1}{kb_{Al}[M]} + \frac{1}{k[M]}[Al] \tag{3}$$

Equation (3) is well fitted by our data (Fig. 2).

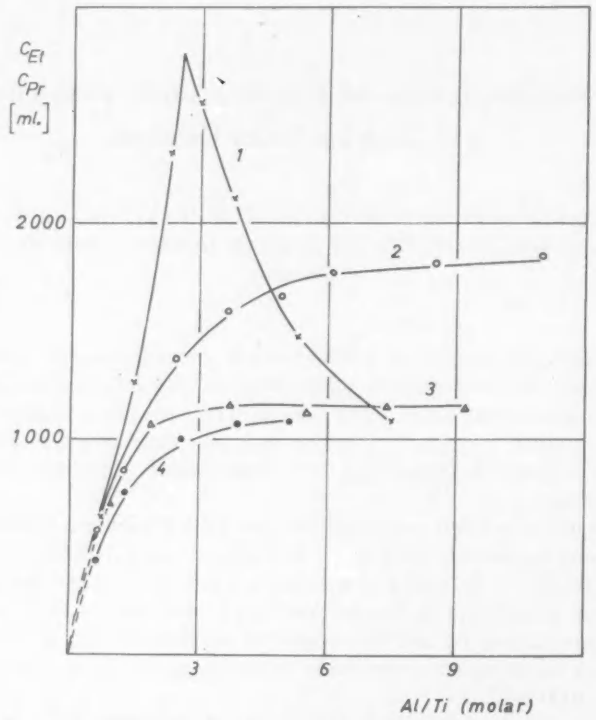

Fig. 1. Monomer consumption (C_{Et}, C_{Pr}) vs. Al/Ti ratio for different catalyst systems: (*1*) $AlR_3/TiCl_4$, $[TiCl_4] = 1.3 \times 10^{-3}$ moles/l., [Et] = 350 torr, 50°C.; (*2*) $AlR_3/TiCl_3$, $[TiCl_3] = 2.6 \times 10^{-3}$ moles/l., [Et] = 450 torr, 50°C.; (*3*) $AlR_3/TiCl_3$, $[TiCl_3] = 4.0 \times 10^{-3}$ moles/l., [Pr] = 355 torr, 56°C.; (*4*) $AlRCl_2/TiCl_4$, $[TiCl_4] = 5.1 \times 10^{-3}$ moles/l., [Et] = 450 torr, 50°C.

On the other hand, maximum curves are obtained with $TiCl_4$ and AlR_3, in fair agreement with the literature[3–9] (Fig. 1, curve *1*). At present, there exist two theories explaining this maximum: one applies a Langmuir-Hinshelwood adsorption mechanism where the monomer competes with the AlR_3 for active sites on the Ti halide surface; the other claims a dependence of polymerization activity on lower valence states (between 3 and 1) of the Ti compound. For a certain Al/Ti ratio there exists a maximum activity (2.5 in our case) connected with a definite valence state. Our results with $TiCl_3$ or $TiCl_4$ and AlR_3 as cocatalyst object to the first and favor the second hypothesis: We never obtained maximum curves with $TiCl_3$ (Fig. 1, curves *2* and *3*) although here, too, a lower valence state than 3 should be reached. This suggests that not the valence state itself but the surface of the lower valent Ti halide is responsible for activity and that the $TiCl_3$ contains a rather stable surface although after reduction the $TiCl_3$ contains a certain amount of lower valent Ti.

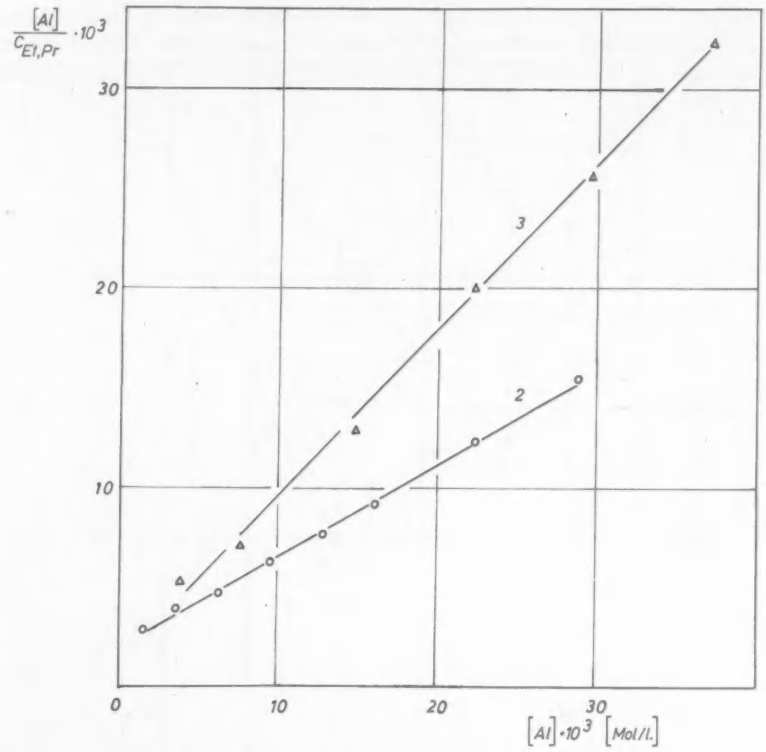

Fig. 2. Plot of curves *2* and *3* of Fig. 1 according to eq. (3).

Al compounds which are unable to reduce $TiCl_4$ below the trivalent state (e.g., AlR_2Cl)[10] do not exhibit maximum curves but give similar curves to those obtained with $TiCl_3$ (Fig. 1, curve *4*).

The temperature dependence is quite different for $TiCl_3$ and $TiCl_4$. Whereas with $TiCl_3$ a normal Arrhenius plot is obtained in the region of 10–60°C. (E_a = 10 kcal./mole) as shown in Figure 3 (curves 1*a* and 1*b*), it is not possible to calculate the activation energy in polymerizations with $TiCl_4$, except for small Al/Ti ratios ($\sim$ Fig. 3). One obtains complex curves for higher ratios and this indicates the influence of temperature on the formation of the catalyst, i.e., on the reduction of the $TiCl_4$ and on the polymerization rate.

With respect to the cocatalysts (Al compounds), they all yield similar adsorption isotherms as shown in Figure 1 curve *3* (in the polymerization of propylene with $TiCl_3$). A comparison of the polymerization activity of the five cocatalysts investigated is given in Figure 4. It shows that $Al(i\text{-}C_4H_9)_3$ and $Al(i\text{-}C_4H_9)_2H$ have comparable high activity, AlR_3 causes polymerization to proceed somewhat more slowly, and AlR_2Cl and $Al_2R_3Cl_3$ are quite

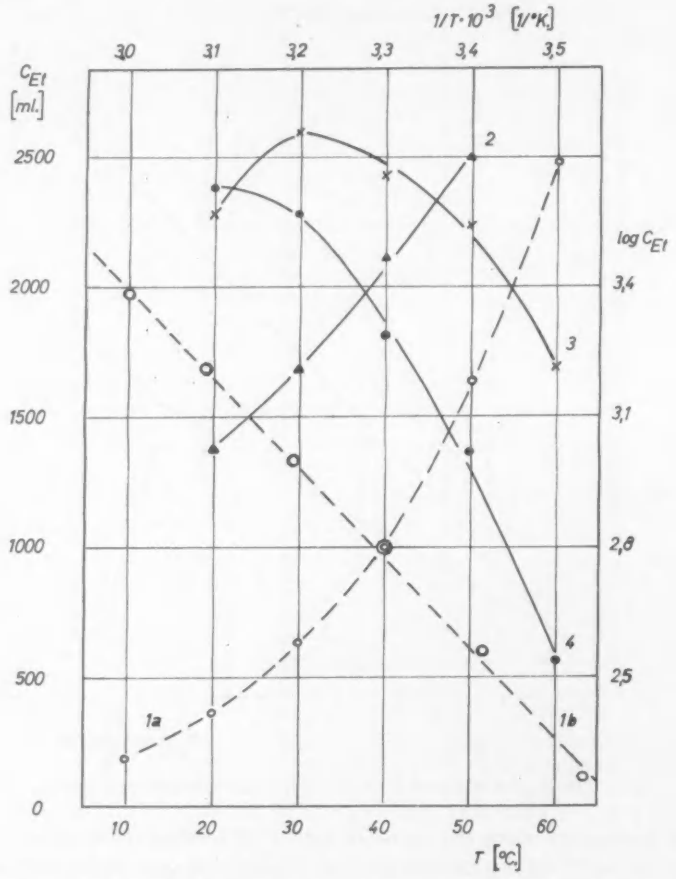

Fig. 3. Ethylene consumption vs. temperature in polymerizations with the systems $AlR_3/TiCl_3$ and $AlR_3/TiCl_4$: (*1a*) $[TiCl_3] = 3.55 \times 10^{-3}$ moles/l., Al/Ti = 3.6, [Et] = 0.038×10^{-3} moles/l.; (*1b*) plot of log C_{Et} vs. $1/T$, conditions as for curve *1a*; (*2*) $[TiCl_4] = 1.3 \times 10^{-3}$ moles/l., Al/Ti = 1.5, [Et] = 0.038×10^{-3} moles/l.; (*3*) $[TiCl_4] = 1.3 \times 10^{-3}$ moles/l., Al/Ti = 3.1, [Et] = 0.034 moles/l.; (*4*) $[TiCl_4] = 1.3 \times 10^{-3}$ moles/l., Al/Ti = 7.8, [Et] = 0.038 moles/l.

low in activity; propylene is not at all polymerized by $AlRCl_2$ under these conditions.

A simultaneous employment of different cocatalysts has interesting features if the two components exert a marked difference in the rate of

polymerization; e.g., in the case of AlR_3 and AlR_2Cl there is a sharp decrease of the rate of polymerization at much higher AlR_3 concentrations than in absence of AlR_2Cl (Fig. 5). This drop can be reversed by renewed

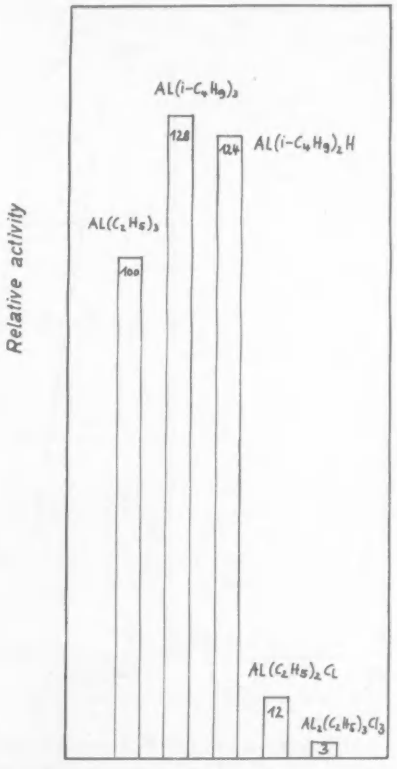

Fig. 4. Comparison of cocatalyst activity in polymerizations of propylene with $TiCl_3$.

addition of AlR_3, showing that there is obviously a reversible adsorption of AlR_2Cl and AlR_3 on the $TiCl_3$ surface (Fig. 6).

The change in slope always occurs at the same constant ratio of both cocatalysts and is, in the regions investigated, independent of $TiCl_3$ concentration, of propylene pressure, or of temperature (Fig. 7). The larger the activity difference of the two cocatalysts, the higher is the ratio $AlR_3/AlR_xCl_{(3-x)}$ at which the change in slope occurs.

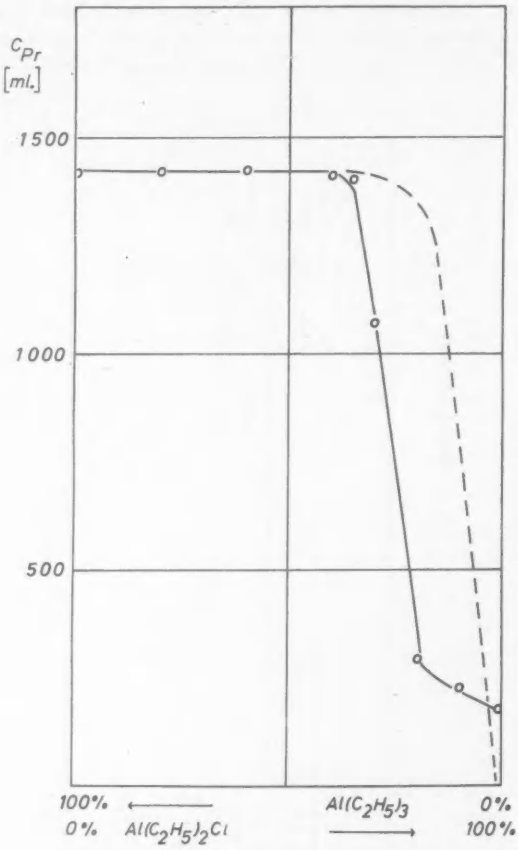

Fig. 5. Plot of (——) propylene consumption vs. cocatalyst composition in polymerizations with the system AlR_3–$AlR_2Cl/TiCl_3$; (- -) consumption calculated for the system AlR_3–$TiCl_3$. Al/Ti = 5.4 (Al = AlR_3 + AlR_2Cl); [$TiCl_3$] = 4.6 × 10^3 moles/l.; [Pr] = 355 torr; 56°C.

With regard to molecular weights or viscosity values the following order in cocatalysts has been observed (Table I): AlR_2Cl > $Al(i\text{-}C_4H_9)_3$ > $Al_2R_3Cl_3 \simeq Al(i\text{-}C_4H_9)H \simeq AlR_3$. This order is not inversely proportional to the activity of the cocatalysts (Fig. 4).

In general, the dependence of Z_η on the Al/Ti ratio shows the well-known decrease with increasing ratio of Al/Ti. For Al concentrations below

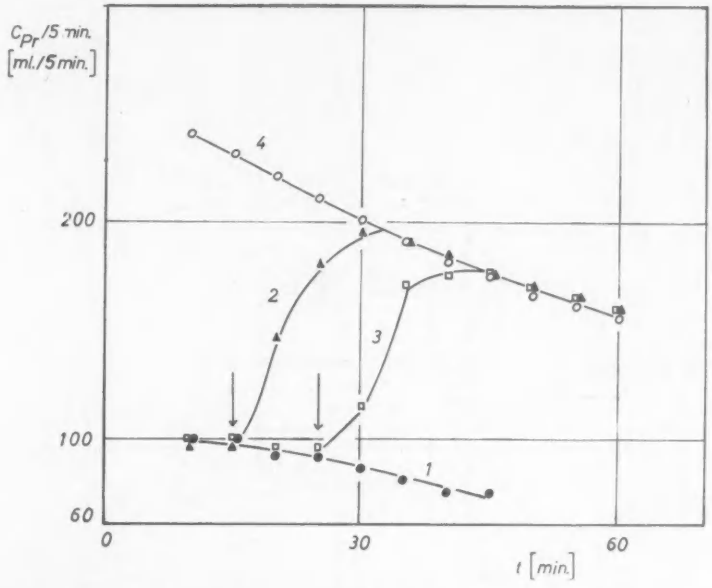

Fig. 6. Change of rate after renewed addition of $AlRCl_2$ in propylene polymerization with the system AlR_3–$AlRCl_2$/$TiCl_3$ at $[TiCl_3] = 4.6 \times 10^{-3}$ moles/l., [Pr] = 355 torr, 56°C.: (*1*) 25×10^{-3} moles/l. $AlR_3 + 15 \times 10^{-3}$ moles/l. $AlRCl_2$; (*2*) same as *1*; after 15 min. addition of 5×10^{-3} moles/l. AlR_3; (*3*) same as *1*, after 25 min. addition of 5×10^{-3} moles/l. AlR_3; (*4*) 30×10^{-3} moles/l. $AlR_3 + 15 \times 10^{-3}$ moles/l. $AlRCl_2$.

TABLE I

Cocatalyst	Z_η
AlR_2Cl	3.55
$Al(i\text{-}C_4H_9)_3$	3.01
$Al_2R_3Cl_3$	2.63
$Al(i\text{-}C_4H_9)_2H$	2.59
AlR_3	2.57

8×10^{-3} moles/l. only, there appears a sharp decrease of viscosity. From here on to higher concentrations Natta's linear relation for $1/Z_\eta^{1.22}$ versus $[Al]^{1/2}$ is obeyed (Fig. 8). (In his case the limiting concentration is 14×10^{-3} moles/l.). The limiting value may be regarded indirectly as a criterion for the purity of the system, since below this concentration the influence of impurities on the cocatalysts becomes valid.

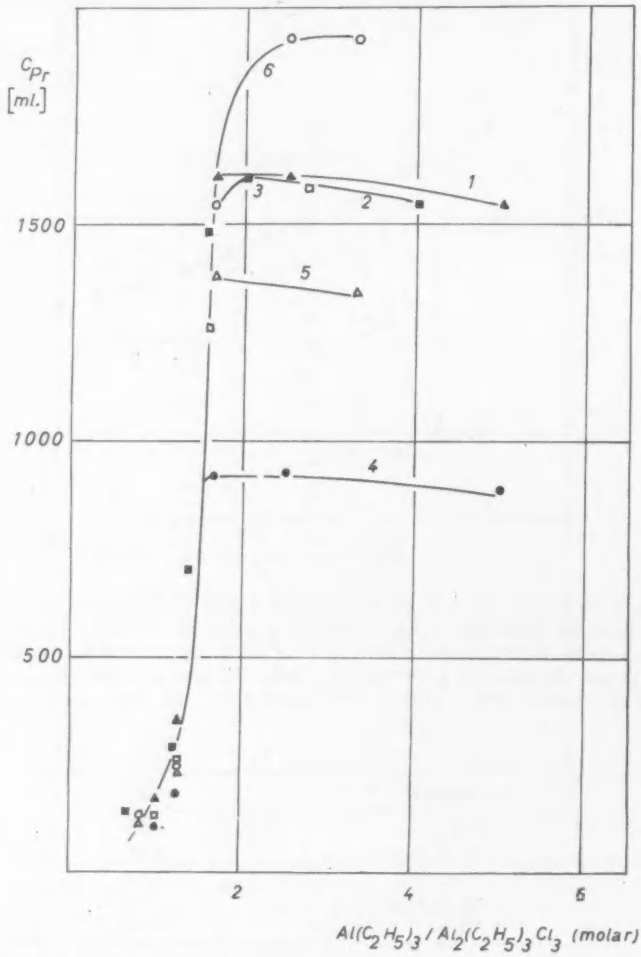

Fig. 7. Activity decrease with changing reaction conditions in propylene polymerization at a constant ratio of $AlR_3/Al_2R_3Cl_3 = 1.5$: (▲): $[TiCl_3] = 4.6 \times 10^{-3}$ moles/l., $[AlR_3] = 25 \times 10^{-3}$ moles/l., [Pr] = 355 torr, 56°C.; (■): $[AlR_3] = 20 \times 10^{-3}$ moles/l.; (□): $[AlR_3] = 10 \times 10^{-3}$ moles/l.; (●): as *1*, $[TiCl_3] = 2.5 \times 10^{-3}$ moles/l.; (△): as *4*, [Pr] = 510 torr. (○): as *1*, 46°C., [Pr] = 510 torr.

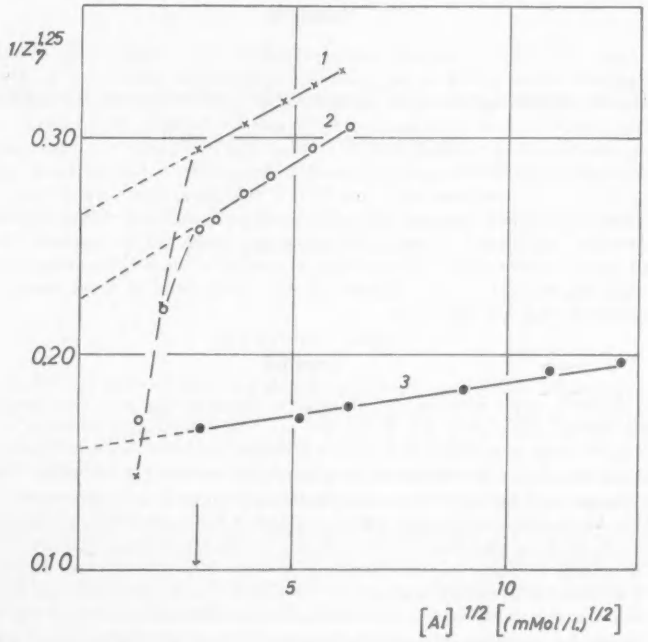

Fig. 8. $1/Z\eta^{1.25}$ vs. $[Al]^{1/2}$ of polypropylenes prepared with $TiCl_3$ and different cocatalysts: (*1*) AlR_3; (2) $Al(i\text{-}C_4H_9)_3$; (*3*) AlR_2Cl.

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Synopsis

The polymerization of ethylene and propylene with Ziegler-Natta catalysts is investigated. Consumption of the gases at concentrations below 1 atm. pressure is measured in a closed system and some kinetic data were obtained. The reliability and stability of the different components of the system is checked. Comparison of the reactivity and the different behavior of Ti(III) and Ti(IV) chloride was made; the resulting data reveal differences in catalyst formation and stability. Calculation of the overall energy of activation is possible for the Ti(III) chloride system. An attempt is made to explain the complex behavior of the Ti(IV) component with varying temperature. Furthermore, mixtures of different cocatalysts are employed to evaluate their compound effect in the reaction. The intrinsic viscosities of the polymers were determined and their dependence on the different Al alkyls, especially at lower concentrations, on conversion, etc. was discussed.

Résumé

On étudie la polymérisation de l'éthylène et du propylène avec des catalyseurs de Ziegler-Natta. La consommation des gaz aux concentrations au-dessous de 1 atm. est mesurée dans un système fermé, et on a obtenu quelques résultats cinétiques. La pureté et la stabilité des différents composants du système est contrôlée. On fait la comparaison entre la réactivité et le comportement différent des chlorure de Ti(III) et Ti(IV); les résultats révèlent des différences dans la formation et la stabilité du catalyseur. On peut calculer l'énergie d'activation totale du système chlorure de Ti(III); une hypothèse est émise en vue d'expliquer le comportement complexe du compostant Ti(IV) avec la variation de température. De plus, on emploie des mélanges de différents co-catalyseurs pour évaluer leur effet composites au cours de la réaction. On mesure et on discute les viscosités intrinsèques des polymères et leur dépendance vis-à-vis des composants du titane, des différents alcoylaluminium, spécialement aux basses concentrations, des degrés, des degrés de conversion, etc.

Zusammenfassung

Die Polymerisation von Äthylen mit Ziegler-Natta-Katalysatoren wird untersucht. Der Gasverbrauch bei Konzentrationen unterhalb 1 Atm. Druck wird in einem geschlossenen System gemessen und einige kinetische Daten werden erhalten. Die Reproduzierbarkeit und Stabilität der verschiedenen Komponenten des Systems wird überprüft. Ein Vergleich der Reaktivität und des Verhaltens von Ti(III)- und Ti(IV)-chlorid wird durchgeführt; die erhaltenen Daten lassen auf Unterschiede in der Bildung und Stabilität des Katalysators schliessen. Für das Ti(III)-chlorid-System kann eine Berechnung der Bruttoaktivierungsenergie durchgeführt werden; es wird versucht, eine Erklärung für die komplexe Temperaturabhängigkeit des Verhaltens der Ti(IV)-Komponente zu geben. Ausserdem werden Mischungen verschiedener Kokatalysatoren zur Ermittlung des zusammengesetzten Einflusses auf die Reaktion verwendet. Die Viskositätszahl der Polymeren und ihre Abhängigkeit von den verschiedenen Al-alkylen, besonders bei niedriger Konzentration, vom umsatz etc. werden gemessen und diskutiert.

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Kinetic Studies in Ethylene Polymerization with Ziegler-Type Catalysts

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INTRODUCTION

Relatively few kinetic investigations have been reported on the polymerization of ethylene with the classical heterogeneous Ziegler-type catalyst systems. Most of the reported studies of such catalyst systems are mainly concerned with the reaction of the catalyst components and the mechanism of the formation of active sites. Comparison of the kinetic studies on polymerization show that some discrepancy still exists among different authors as to the order of the polymerization rate with respect to the ethylene concentration, even though closely related catalyst systems had been used. At fixed catalysts compositions, Feilchenfeld and Jeselson[1] as well as Ludlum[2] found a strict first-order relationship, whereas a second-order dependence of rate on monomer concentration was reported by McGowan and Ford[3] and Gilchrist.[4]

The present investigation of ethylene polymerization initiated with a catalyst system consisting of diisobutylaluminum hydride (DIBAH) and titanium tetrachloride was undertaken in order to determine the dependence of the rate of polymerization on monomer concentration as well as to investigate the participation of hydrogen in the polymerization mechanism.

EXPERIMENTAL

All polymerizations were carried out in *n*-heptane at 40°C. with the same initial concentrations of catalyst components, 1.5 mmoles/l. DIBAH and 2.5 mmoles/l. $TiCl_4$. The catalyst components were reacted at these concentrations at 0°C. and the mixture was then aged under a nitrogen blanket for 15 min. At the end of the aging period the nitrogen was pumped off and the catalyst suspension heated to 40°C. and kept at this temperature by circulating water from a thermostated bath through the jacket of the reaction flask.

The three-necked reaction flasks, 500 and 1000 ml., were equipped with a Lew type magnetic stirrer, gas inlet, and a stopcock with the free end closed by a self-sealing rubber stopper, the latter being used for the transfer of the catalyst components from the stock solutions by means of gas-tight syringes. The gas inlet could be connected with either one of the lines for

vacuum, nitrogen, hydrogen, deuterium, or ethylene. The rate of ethylene feed was measured with a flowmeter of the floating ball type with a calibrated range of 1.2–50.0 mmoles/min. The ethylene pressure, before entering the flowmeter, was held constant at 770 Torr with a mercury bubbler. This pressure corresponds to the total pressure inside the reaction flask in all experiments, the small pressure drop across the flowmeter being neglected. All gases, except deuterium, were passed through a heated column filled with BTS catalyst (B.A.S.F.) for the removal of traces of oxygen and then through a silica gel column.

With the vapor pressure of heptane at 40°C. being 90 Torr, the maximum ethylene pressure investigated was 680 Torr. Lower ethylene pressure was obtained in two ways: by the addition of inert gases such as nitrogen, hydrogen, or deuterium, and also by executing the polymerization with a starved ethylene feed. In the first case the particular gas was introduced into the reaction flask up to the desired partial pressure after aging of the catalyst suspension and prior to the feeding of the ethylene. In the second method the flow rate of the ethylene was preset and maintained constant throughout the experiment. The adjusting pressure in the reaction flask was measured in intervals. This latter experiment will be referred to as reduced pressure runs.

After deactivation of the catalyst with methanol the polymer was thoroughly washed and dried in vacuum at 60°C.

For infrared measurements on the polymers a Perkin-Elmer 237 double-grating spectrophotometer was used. The absorbance in the pertinent regions was determined on compression molded films of three thicknesses in the range of 0.07–0.25 mm., a compensation method with polymethylene wedge[5] being used.

RESULTS AND DISCUSSION

Rate of Polymerization

With the start of the ethylene feed the polymerizations always began immediately. Meaningful flowmeter readings could not be obtained during the first few minutes due to experimental considerations, since during this interval the reaction flask had to be filled with ethylene and the stationary ethylene concentration in the heptane had to establish itself. After this adjustment period, the rate of polymerization levelled out and remained constant for a prolonged period. A decrease of the polymerization rates was usually observed at polymer concentrations higher than 1 mole/l., and this decrease was interpreted as caused mainly by stirring difficulties and also by the occlusion of part of the catalyst in the precipitating polymer particles. The results of some representative experiments are shown in Figure 1, where the cumulative polymer yields are plotted versus time. For kinetic evaluations the slopes of the linear parts of these plots were used to represent the rates of polymerization at the particular experimental conditions.

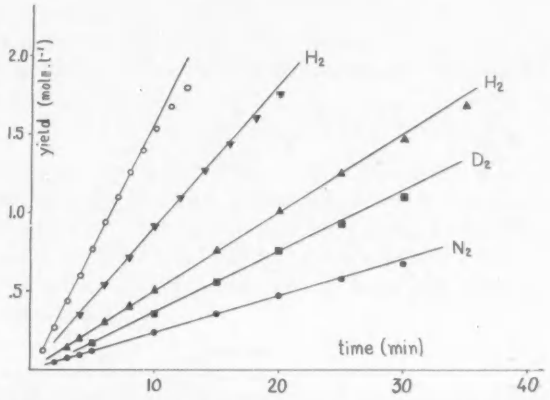


Fig. 1. Polymerization of ethylene in the presence of different gases (The sum of the partial pressures being 680 Torr): (○) no gas added; (▼) 161 Torr hydrogen pressure; (▲) 304 Torr hydrogen pressure; (■) 390 Torr deuterium pressure; (●) 474 Torr nitrogen pressure.

In the experiments at reduced pressure, where a starved ethylene feed was used, corresponding behavior was observed. The ethylene pressure inside the reaction flask increased during the first interval and remained constant for such a time until the accumulating polymer caused a decrease in the rate of polymerization.

According to the four different ways by which changes in the partial pressures of the ethylene have been accomplished experimentally, the rate data can be grouped into four sets: experiments at reduced pressure, and experiments with the addition of nitrogen, hydrogen, and deuterium. In none of these four sets of data a direct proportionality between the rate of polymerization R_p and the ethylene pressure, p_E, could be observed. Therefore, a strict first-order dependence of the rate of polymerization with respect to ethylene concentration cannot be valid for the investigated catalyst system and it was found indeed that the experimental data could be represented best by assuming a mixed first and second-order dependence of the form

$$R_p = Kp_E^2/(1 + K'p_E) \tag{1}$$

In Figure 2 the experimental data are represented according to

$$p_E/R_p = A + B(1/p_E) \tag{2}$$

a slightly transformed form of eq. (1) which yields a more convenient graphic representation.

According to eq. (1), the rate of polymerization will be first-order with respect to ethylene pressure as long as the pressure remains high enough in order to make $K'p_E$ large compared to unity. At low ethylene pressures the reverse condition will be valid, and the rate will approach a second-

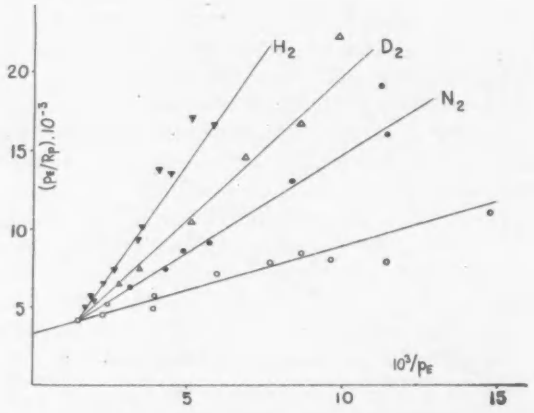


Fig. 2. The influence of different gases on the pressure dependence of the rate of polymerization: (○) no gas added; (●) nitrogen; (△) deuterium; (▼) hydrogen.

order dependence. In order to bring the kinetic results in agreement with the concept of the polymerization mechanism, a pressure-dependent step has to be considered which becomes of increasing importance with decreasing pressure.

Without specifically confining the discussion at the moment to one of the propagation mechanisms presented in the literature, it might be generalized that monomer is added to an organometallic compound which comprises the active center and that chain growth proceeds thereafter through the addition of further monomer units by an anionic polymerization mechanism.

$$\overset{(+)\ (-)}{\text{Cat}\ \text{CH}_2\text{—CH}_2\text{—(CH}_2\text{—CH}_2)_n\text{—R}} + \text{CH}_2\text{=CH}_2 \xrightarrow{k_p} \overset{(+)\ (-)}{\text{Cat}\ \text{CH}_2\text{—CH}_2\text{—(CH}_2\text{—CH}_2)_{n+1}\text{—R}} \quad (3)$$

The growth of an individual polymer chain can be terminated either by a transfer reaction with the monomer

$$\overset{(+)\ (-)}{\text{Cat}\ \text{CH}_2\text{—CH}_2\text{—R}} + \text{CH}_2\text{=CH}_2 \xrightarrow{k_{tr}} \overset{(+)\ (-)}{\text{Cat}\ \text{CH}_2\text{—CH}_3} + \text{CH}_2\text{=CH}_3\text{—R} \quad (4)$$

or by a spontaneous termination reaction involving the transfer of a hydride ion

$$\overset{(+)\ (-)}{\text{Cat}\ \text{CH}_2\text{—CH}_2\text{—R}} \xrightarrow{k_0} \overset{(+)\ (-)}{\text{Cat}\ \text{H}} + \text{CH}_2\text{=CH—R} \quad (5)$$

In both cases unreactive polymer chains with a terminal vinyl group are formed. Reaction (4) is a true transfer reaction, with the resulting new catalyst–alkyl bond identical in reactivity to the one formerly present. The formation of a catalyst–hydride bond in reaction (5) can be considered

as a termination step, since this bond will not be immediately available for further chain propagation but will have to be alkylated first, a reaction step which might require a higher activation energy than the one corresponding to the addition of monomer to a catalyst–alkyl bond.

$$\overset{(+)\ (-)}{\text{Cat H}} + \text{CH}_2{=}\text{CH}_2 \xrightarrow{k_i} \overset{(+)\ (-)}{\text{Cat CH}_2}\text{—CH}_3 \tag{6}$$

From the above mechanism it follows that two different active catalyst sites are present in the system, propagating sites with metal–alkyl bonds of the concentration c_E^*, and latent sites with metal–hydride bonds of the concentration c_H^*. The total concentration of active sites, c_0^*, can be assumed to remain constant, since identical catalyst preparations were used in all experiments.

$$c_0^* = c_E^* + c_H^* \tag{7}$$

The ratio of both active sites is then given by the stationary-state condition

$$k_s c_E^* = k_i p_E c_H^* \tag{8}$$

where the left side corresponds to the formation of latent sites by spontaneous termination and the right side to the realkylation of the thereby resulting metal–hydride bonds. With the rate of propagation given by

$$R_p = k_p p_E c_E^* \tag{9}$$

one obtains finally

$$R_p = (k_i/k_s) k_p c_0^* p_E^2 / [(k_i/k_s) p_E + 1] \tag{10}$$

in agreement with the experimentally found relationship, eq. (1).

In experiments with the addition of hydrogen, the observed rates of polymerization were found to be decreased far more strongly than corresponding to the decrease in the partial pressure of the ethylene, a result that indicates the participation of the hydrogen in the polymerization mechanism. Such a participation of the hydrogen, involving a transfer reaction according to

$$\overset{(+)\ (-)}{\text{Cat CH}_2}\text{—CH}_2\text{—R} + \text{H}_2 \xrightarrow{k_H} \overset{(+)\ (-)}{\text{Cat H}} + \text{CH}_3\text{—CH}_2\text{—R} \tag{11}$$

was proposed by Natta et al.[6] as derived from the molecular weight decreasing effect of the added hydrogen in the polymerization of propylene. The above mechanism could be confirmed by the results obtained in experiments with deuterium addition where infrared analysis of the polymers revealed the presence of CH_2D endgroups.

In the kinetic treatment of experiments with hydrogen addition, an additional term has to be introduced in the left side of eq. (8) in order to take care of the additional formation of latent catalyst sites by the transfer reaction with hydrogen

$$k_s c_E^* + k_H c_E^* p_H = k_i p_E c_H^* \tag{12}$$

The derived rate expression is then given by

$$R_p = k_i k_p c_0^* p_E^2/(k_s + k_i p_E + k_H p_H) \tag{13}$$

and can be transformed into the form of eq. (1) since under the experimental conditions the concentrations of ethylene and hydrogen are related by the constancy of the sum of the partial pressures in all experiments.

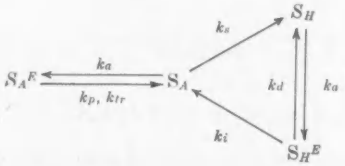
In the kinetic treatment of experiments with deuterium addition, two stationary-state conditions have to be used, one with respect to the concentration of metal–hydride bonds resulting from the spontaneous termination, and the other considering the concentration of metal–deuteride bonds resulting from the transfer reaction with the deuterium. Also in this case a rate equation of the form of eq. (1) is obtained.

The kinetic scheme proposed so far explains the observed mixed order in the dependence of the rate on ethylene pressure at all experimental conditions but the one where the ethylene was diluted with nitrogen. The pronounced lower rate in the latter case as compared with experiments at reduced pressure can only be explained with the assumption that adsorption effects play an important role in the polymerization mechanism since any other participation of nitrogen is hard to imagine. It is therefore necessary to modify the kinetic treatment such as to omit the tacit assumption that the rate of chain propagation is the slowest and therefore the rate-determining step in the polymerization mechanism.

It is generally assumed that in polymerizations with heterogeneous catalyst systems of the Ziegler-Natta type chain propagation proceeds by insertion of monomer units into metal–alkyl bonds, such bonds being initially formed during the reaction of the catalyst components and being present as a surface phase of the dispersed titanium trichloride. It has not been clarified yet whether the active sites involve alkylated titanium compounds only[7] or whether the active centers are bimetallic complexes consisting of titanium and aluminum atoms linked together by alkyl bridges.[8,9] Regardless of the concept used, the monomer molecule has to be adsorbed on the catalyst site previous to its insertion into the growing polymer chain. If it is assumed that this adsorption process is the rate-determining step, the following insertion step proceeding very fast, only a small fraction of the total number of catalyst sites will be occupied by the ethylene, the majority of the sites being vacant.

In the following kinetic treatment the number of catalyst sites per unit area of catalyst surface will be expressed by S with the subscripts A and H in order to distinguish between sites with active alkyl bonds and sites with latent hydride bonds, respectively. The superscripts E, N, H, and D will denote the kind of gas adsorbed, corresponding to ethylene, nitrogen, hydrogen, and deuterium, vacant sites remaining without a superscript.

The kinetic scheme for polymerizations in the absence of any diluting gas can be represented by



(14)

where k_a and k_d are the rate constants for the adsorption and the desorption of the ethylene, and k_{tr} is the rate constant for the transfer reaction with monomer. It is assumed as a simplification that catalyst sites with alkyl bonds are vacated only by a propagation or a transfer reaction and not by desorption. A change of the catalyst site from one with an alkyl bond to one with a hydride bond will not change the adsorptive site and therefore the same rate constants for the adsorption process can be used in both cases.

At least during the time interval where the rate of polymerization was found to remain unchanged, the number of catalyst sites can be assumed to stay constant.

$$S = S_A + S_H + S_A{}^E + S_H{}^E \tag{15}$$

Since it follows from the assumption of an adsorption controlled polymerization mechanism that at low ethylene pressures the number of catalyst sites occupied by adsorbed ethylene will be negligibly small compared with the number of vacant sites, eq. (15) can be simplified to

$$S/S_A{}^E = S_A/S_A{}^E + S_H/S_A{}^E \tag{16}$$

The ratios on the right side of eq. (16) can be obtained with the assumption of a stationary state being established with respect to the concentrations of the different catalyst sites as expressed by eqs. (17)–(20).

$$dS_A/dt = (k_p + k_{tr})S_A{}^E + k_iS_H{}^E - k_aS_Ap_E - k_sS_A = 0 \tag{17}$$

$$dS_H/dt = k_sS_A + k_dS_H{}^E - k_aS_Hp_E = 0 \tag{18}$$

$$dS_A{}^E/dt = k_aS_Ap_E - (k_p + k_{tr})S_A{}^E = 0 \tag{19}$$

$$dS_H{}^E/dt = k_aS_Hp_E - (k_i + k_d)S_H{}^E = 0 \tag{20}$$

The necessary ratios are then given by

$$S_A/S_A{}^E = (k_p + k_{tr})/k_ap_E \tag{21}$$

$$S_H/S_A{}^E = k_s(k_p + k_{tr})(k_i + k_d)/k_ik_a{}^2p_E{}^2 \tag{22}$$

Combining eqs. (16), (21), and (22) together with the expression for the rate of polymerization, eq. (23),

$$R_p = k_pS_A{}^E \tag{23}$$

one obtains the final rate expression which is of the same form as the experimentally found eq. (2)

$$p_E/R_p{}^0 = A_0 + B_0(1/p_E) \tag{24}$$

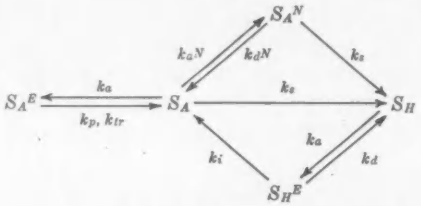
with

$$A_0 = (k_p + k_{tr})/k_a k_p S \tag{25}$$

and

$$B_0 = k_s(k_p + k_{tr})(k_i + k_d)/k_i k_a^2 k_p S \tag{26}$$

The kinetic scheme of eq. (14) has to be modified somewhat for polymerization experiments carried out in the presence of nitrogen in order to account for the occupation of catalyst sites by adsorbed nitrogen molecules:



(27)

where the rate constants $k_a{}^N$ and $k_d{}^N$ correspond to the adsorption and desorption of the nitrogen. Equations (16) and (23) remain valid also in this case, and only the set of stationary-state equations has to be adjusted to the changed polymerization conditions according to the scheme of eq. (27). Without going into details of the rather simple algebra involved, the final rate expression obtained is of the form

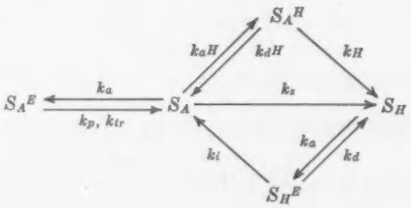
$$p_E/R_p{}^N = p_E/R_p{}^0 + B_N\,(p_N/p_E) \tag{28}$$

with

$$B_N = [k_s(k_i + k_d)(k_p + k_{tr})/(k_s + k_d{}^N)k_i k_a k_p S]\;(k_a{}^N/k_a) \tag{29}$$

The eq. (28) shows that the rate of polymerization will be lower in the presence of nitrogen as compared to the rate at the same ethylene pressure but obtained in the absence of a diluting gas. Since in all experiments the sum of the partial pressures of ethylene and diluting gas is kept constant, the second quotient of the last term in eq. (28) can be expressed solely by the ethylene pressure and an expression corresponding to the form of eq. (2) is obtained.

The kinetic scheme for experiments conducted in the presence of hydrogen is essentially the same as the one shown in eq. (27) wherein only $S_A{}^N$ has to be replaced by $S_A{}^H$ and the rate constant leading therefrom to S_H has to be changed to k_H, the rate constant for the transfer reaction with hydrogen.



(30)

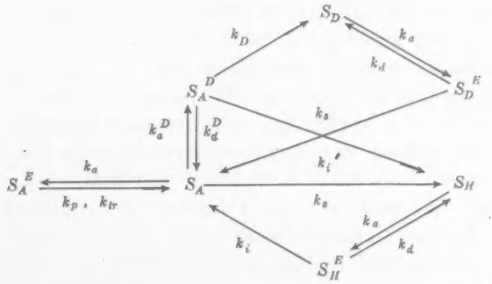
The evaluation is identical to the previous one and yields the rate equation

$$p_E/R_p^H = p_E/R_p^0 + B_H(p_H/p_E) \tag{31}$$

with

$$B_H = [k_H(k_i + k_d)(k_p + k_{tr})/(k_H + k_d^H)k_i k_a k_p S](k_a^H/k_a) \tag{32}$$

With the presence of deuterium in the polymerization system, catalyst deuteride bonds as well as catalyst hydride bonds are formed, the former by a transfer reaction, $k_D S_A^D$, the latter by spontaneous termination. The realkylation of both types of latent bonds might differ due to the isotope effect, and therefore two different rate constants, k_i' and k_i, have to be used. The kinetic scheme can be represented according to eq. (33):



(33)

The spontaneous termination of S_A^D sites leading to S_H sites, as represented in eq. (33), is not quite correct, since the resulting catalyst sites would be S_H^D sites which are in adsorption equilibrium with S_H sites, but this simplification turns out to be rather unimportant. The mathematical evaluation of the kinetic scheme of eq. (33) is similar to previous evaluations, only eq. (16) has to be enlarged by one term which considers the presence of vacant catalyst sites with deuteride bonds.

$$S/S_A^E = S_A/S_A^E + S_H/S_A^E + S_D/S_A^E \tag{34}$$

The final rate equation is then given by

$$p_E/R_p^D = p_E/R_p^0 + B_D(p_D/p_E) \tag{35}$$

with

$$B_D = (k_p + k_{tr})/(k_D + k_s + k_d^D)k_a k_p S + [k_s + k_D(k_i' + k_d)/k_i'](k_a^D/k_a) \tag{36}$$

Methyl Content of Polymers

In order to test the validity of the kinetic model of a polymerization mechanism the number-average molecular weights and their dependence on the polymerization conditions are usually used in addition to rate measurements. In the case of ethylene polymerization with metal-organic catalyst

systems the application of number-average molecular weights meets two difficulties. The calculation of number-average molecular weights from conveniently obtainable viscosity data might be subjected to rather big errors, if changes in the polymerization conditions are accompanied by changes in the molecular weight distributions, since the latter are in general rather broad, ratios of $\bar{M}_w/\bar{M}_n$ higher than ten being usual. It is very likely that in experiments with increasing predominance of transfer reactions the $\bar{M}_w/\bar{M}_n$ ratios will decrease successively, and the molecular weight–viscosity relationship will change in a corresponding but unfortunately unknown way.

Direct determinations of number-average molecular weights are rather tedious, and also in this case a difficulty of principal nature might arise caused by the presence of branched polymer chains. In free-radical polymerization where the formation of branched polymer chains involves a transfer reaction between growing macroradicals and polymer chains, the number-average molecular weight is not influenced since both, the number of free radicals and the amount of converted monomer remains unchanged. In olefin polymerization with Ziegler-Natta catalysts it is generally assumed that branches are introduced by a copolymerization mechanism whereby polymer chains released from the catalyst with a terminal vinyl group will act as a comonomer. It is evident that in this case the branched polymer molecule consists of several kinetic chains which are not counted in the molecular weight determination and are therefore omitted from the kinetic evaluation.

According to the reaction mechanism given by the eqs. (3)–(6), and (11), methyl groups will be formed by transfer reactions with monomer or with hydrogen, and also in the realkylation step of catalyst hydride bonds. This statement can be expressed mathematically by

$$d[\mathrm{CH_3}]/dt = k_{tr}S_A{}^E + k_tS_H{}^E + k_HS_A{}^H \tag{37}$$

an expression which has to be valid for all experimental conditions. Dividing eq. (37) by the rate of polymerization, eq. (23), yields the number of methyl groups per ethylene unit polymerized.

$$N_{\mathrm{CH_3}} = k_{tr}/k_p + (k_t/k_p)(S_H{}^E/S_A{}^E) + (k_H/k_p)(S_A{}^H/S_A{}^E) \tag{38}$$

Equation (38) only takes care of the number of methyl groups formed during the stationary state of the polymerization and therefore two errors might be introduced by the experimental evaluation: (*a*) the unknown amount of methyl groups formed in the deactivation step, corresponding to the number of metal–alkyl bonds present at this moment, and (*b*) the unknown number of methyl groups introduced in the initiation step which are derived from the alkyl groups of the aluminum alkyl. Infrared results indicated that under experimental conditions the first error is negligible since deactivation of the polymerization reaction with D_2O did not yield any detectable amount of CH_2D groups in the polymer. From this

result it might be concluded that also the second error will remain inside the range of accuracy of the methyl group determination.

The ratios of the number of catalyst sites, necessary for the evaluation of eq. (38), can be obtained from the proper set of stationary state equations. For experiments carried out at reduced pressure the set of eqs. (17)–(20) yields

$$S_H^E/S_A^E = k_s(k_p + k_{tr})/k_s k_a p_E \tag{39}$$

In this case the last term on the right side of eq. (38) is zero and one obtains by substituting eq. (39)

$$N_{CH_3}^0 = k_{tr}/k_p + \beta_0(1/p_E) \tag{40}$$

with

$$\beta_0 = k_s(k_p + k_{tr})/k_p k_a \tag{41}$$

With the addition of different gases to the polymerization system the following expressions for the methyl contents of the polymers apply.

Nitrogen addition:

$$N_{CH_3}^N = N_{CH_3}^0 + \beta_N(p_N/p_E) \tag{42}$$

with

$$\beta_N = [k_s(k_p + k_{tr})/(k_s + k_d^N)k_p](k_a^N/k_a) \tag{43}$$

Hydrogen addition:

$$N_{CH_3}^H = N_{CH_3}^0 + 2\beta_H(p_H/p_E) \tag{44}$$

with

$$\beta_H = [k_H(k_p + k_{tr})/(k_H + k_d^H)k_p](k_a^H/k_a) \tag{45}$$

Deuterium addition:

$$N_{CH_3}^D = N_{CH_3}^0 + \beta_D(p_D/p_E) \tag{46}$$

with

$$\beta_D = [k_s(k_p + k_{tr})/(k_D + k_s + k_d^D)k_p](k_a^D/k_a) \tag{47}$$

Since the ratios of the partial pressures can always be substituted by $p_t/p_E - 1$, where p_t is the sum of the partial pressures, a linear relationship between the methyl content and the reciprocal partial pressure of the ethylene should be observed in all cases. In Figure 3 the absorbance per millimeter film thickness at 7.26 μ, corresponding to the methyl contents of the polymers, is plotted versus the reciprocal ethylene pressure, and the demanded linear relationships are obtained.

From the kinetic equations it can be derived that the rates of polymerization and the methyl contents of the polymers are correlated by

$$B_0/\beta_0 = B_N/\beta_N = B_H/\beta_H = (k_i + k_d)/k_i k_a S \tag{48}$$

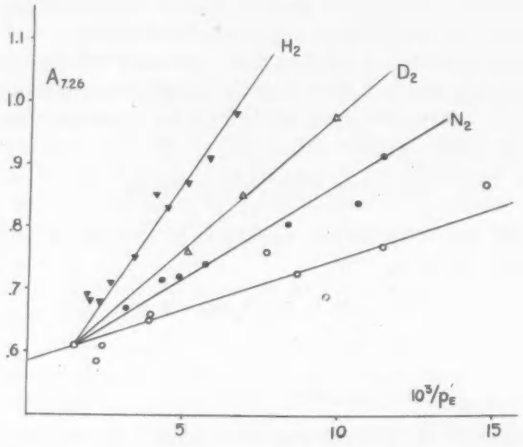


Fig. 3. The influence of different gases on the pressure dependence of the methyl content of the polymers: (○) no gas added; (●) nitrogen, (△) deuterium, (▼) hydrogen. $A_{7.26}$ corresponds to the absorbance per millimeter film thickness at 7.26 μ.

This relationship can be tested without introducing errors due to incorrect infrared calibrations, by replacing the methyl contents by the corresponding infrared absorbances. In the Figures 4 and 5 the differences of the p_E/R_p values and of the methyl absorbances, as referred to experiments at reduced pressure, are plotted versus the ratios of the partial pressures, the slopes of the straight lines yielding the B values and the β values, respectively.

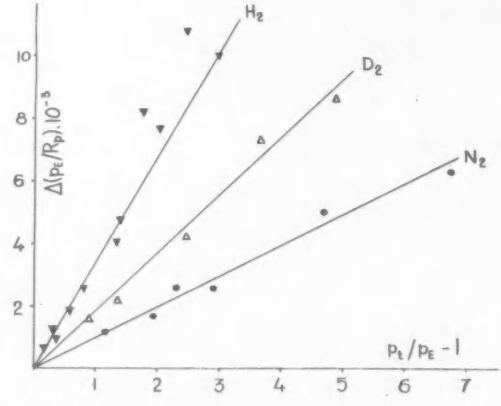


Fig. 4. Rates of polymerization as referred to reduced pressure experiments at corresponding ethylene pressures.

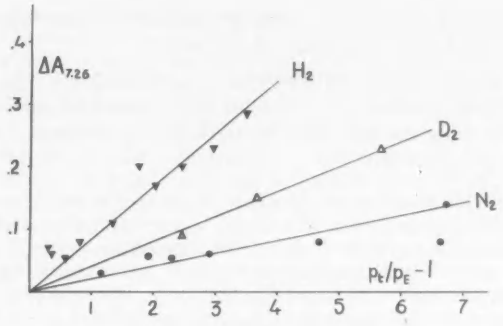


Fig. 5. Methyl contents of polymers as referred to reduced pressure experiments at corresponding ethylene pressures.

The ratio of B_0/β_0, as obtained from Figures 2 and 3, was found to be 3.4×10^4, in good agreement with a value of 4.7×10^4 as obtained for B_N/β_N. The value representing the experiments with hydrogen addition is still of the same order of magnitude, $B_H/\beta_H = 7.9 \times 10^4$, but the ratio is too large, approximately by a factor of two. The latter result might be caused by an oversimplified kinetic treatment.

Deuterium Content of Polymers

According to the transfer mechanism of hydrogen as proposed by Natta, it was to be expected that by replacing the hydrogen by deuterium the presence of CH_2D groups in the polymer should be detectable by infrared analysis. Infrared measurements revealed the presence of two absorption peaks not being found in polyethylene prepared in the absence of deuterium. The first peak, at 4.62 μ, could be assigned to the presence of CH_2D groups as derived from infrared analysis of copolymers of ethylene with 1-undecene-11-d_1. The accompanying second peak at 4.70 μ, which always was much stronger than the first one, had to be assigned to the presence of CHD groups.[10] The presence of CHD groups in the polymer was somewhat surprising and their formation could only be explained with the assumption of a hydrogen-deuterium exchange reaction taking place, most likely involving the β-hydrogen of the growing chain.

The choice of the β-hydrogen being involved in the exchange reaction is supported by two experimental results. It was found by de Vries[11] that decomposition of titanium alkyls occurs only if the alkyl groups possess a hydrogen on the β-carbon, a result which shows the exceptional reactivity of the hydrogen attached at this place. The other supporting result was reported by Natta,[12] who found that propylene polymerization in the presence of hydrogen is always accompanied by a pronounced decrease in the steric purity of the polymer. This experimental result follows directly from the proposed exchange reaction involving the hydrogen on the β-carbon. This exchange reaction, under the experimental conditions of

Natta, is a hydrogen–hydrogen exchange, and a steric rearrangement of the last monomer unit can, therefore, take place.

From the kinetic scheme representing the polymerization in the presence of deuterium, eq. (33), expressions for the content of CH_2D and CHD groups in the polymer can also be obtained; however, these will not provide any new conclusions.

The experimental work of this paper was started while the author was still affiliated with the Research Center of Koppers Company, Incorporated, Monroeville, Pa. In this connection the author would like to express his appreciation to Drs. E. M. Fettes and R. A. V. Raff for their stimulating discussions in the earlier stages of this work. The continuation and extension of this work at the Camille Dreyfus Laboratory was made possible through the sponsorship of the Celanese Corporation of America.

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Synopsis

The polymerization of ethylene with a heterogeneous catalyst system consisting of titanium tetrachloride and diisobutylaluminum hydride was investigated in the pressure range below 1 atm., in the presence of nitrogen, hydrogen, deuterium, and in the absence of a diluting gas. The experimental rate equation was of the form $R_p = Kp_E^2/(1 + K'p_E)$, both constants, K and K', being strongly dependent on the diluting gas used. The methyl content of the polymers increased with a decrease of the partial pressure of the ethylene, the rate of decrease being also influenced by the gas used for dilution. The observed pressure dependences of both, the rates of polymerization and the methyl contents of the polymer, could be explained with two basic assumptions: (*1*) the polymerization mechanism is adsorption-controlled, the adsorption of the ethylene on the catalyst sites being the rate-determining step, whereas the insertion of the adsorbed monomer unit into the growing chain proceeds very fast; (*2*) the propagating metal–alkyl bonds will terminate spontaneously, thereby yielding metal–hydride bonds which have to be realkylated in a pressure-dependent step in order to participate again in the polymerization process. In experiments with the addition of deuterium an exchange reaction was observed, very likely involving the hydrogen on the β-carbon of the growing chain, an effect which will explain the observed decrease in the steric purity of polypropylene polymerized in the presence of hydrogen.

Résumé

On a étudié la polymérisation de l'éthylène au moyen d'un catalyseur hétérogène contenant du tétrachlorure de titane et de l'hydrure de diisobutylaluminium dans un

domaine de pression inférieur à une atmosphère, en présence d'azote, d'hydrogène, de deutérium, et en absence de gaz diluant. L'équation de vitesse expérimentale est de la-forme $R_p = Kp_E^2/(1 + K'p_E)$, les deux constantes, K et K' dépendant fortement du gaz diluant employé. La teneur en groupes méthyles du polymère augmente avec la diminution de la pression partielle de l'éthylène, la vitesse de diminution étant aussi influencée par le gaz employé pour la dilution. On explique les dépendances vis-à-vis de la pression des vitesses de polymérisation et des teneurs en méthyle du polymère au moyen de deux hypothèses de base. (*1*) Le mécanisme de polymérisation est sous le contrôle de l'adsorption, l'adsorption d'éthylène sur les sites catalyseurs étant l'étape déterminante de vitesse, tandis que l'insertion de l'unité monomérique adsorbée dans la chaîne en croissance se fait tres rapidement. (*2*) Les liens de propagation métal-alcoyle sont terminés spontanément tandis que les liens métal–hydrure (formés) sont à nouveau alcoylés dans une étape dépendant de la pression afin de participer à nouveau au processus de polymérisation. On a observé une réaction d'échange dans les expériences effectuées avec addition de deutérium, ce qui implique très vraisemblablement de l'hydrogène sur le carbone en bèta de la chaîne en croissance; cet effet explique la diminution observée dans la pureté stérique du polypropylène polymérisé en présence d'hydrogène.

Zusammenfassung

Die Polymerisation von Äthylen mit einem heterogenen Katalysatorsystem aus Titantetrachlorid und Diisobutylaluminiumhydrid wurde im Druckbereich unterhalb einer Atmosphäre in Gegenwart von Stickstoff, Wasserstoff, Deuterium und in Abwesenheit eines Verdünnungsgases untersucht. Die experimentelle Geschwindigkeitsgleichung besass die Form $R_p = Kp_E^2/(1 + K'p_E)$, wobei beide Konstanten, K und K', eine starke Abhängigkeit vom verwendeten Verdünnungsgas zeigten. Der Methylgehalt der Polymeren nahm mit fallendem Partialdruck des Äthylens zu und auch die Geschwindigkeit der Abnahme war vom Verdünnungsgas abhängig. Die beobachtete Druckabhängigkeit der Polymerisationsgeschwindigkeit und des Methylgehalts des Polymeren kann durch zwei Grundannahmen erklärt werden. (*1*) Der Polymerisationsmechanismus ist adsorptionskontrolliert, die Adsorption von Äthylen an die Katalysatoroberfläche ist der geschwindigkeitsbestimmende Schritt, während die Einfügung des adsorbierten Monomerbausteins in die wachsende Kette sehr schnell verläuft. (*2*) Die wachstumsfähige Metallalkylbindung erfährt einen spontanen Abbruch und bildet dabei Metall-Hydridbindungen, welche zur Wiederteilnahme am Polymerisationsprozess in einem druckabhängigen Schritt realkyliert werden müssen. Bei Versuchen mit Deuteriumzusatz wurde eine Austauschreaktion, wahrscheinlich unter Teilnahme des Wasserstoffs am β-Kohlenstoffatom der wachsenden Kette, beobachtet. Durch diesen Effekt lässt sich die bei der Polymerisation von Propylen in Gegenwart von Wasserstoff beobachtete Abnahme der sterischen Reinheit erklären.

Discussion

L. S. Rayner (*I.C.I. Ltd., Herts., Great Britain*): I have two questions to ask Dr. Schindler:

(*1*) In his work on the effect of nitrogen on ethylene polymerization has he taken account of the solubility of nitrogen in the diluent? Has he in fact calculated or measured the concentration of ethylene in the liquid phase and correlated this with the polymerization rate?

(*2*) Dr. Schindler quoted that a lower stereospecificity is obtained in propylene polymerization in the presence of hydrogen and he suggested a mechanism to account for this. I question whether in fact the stereospecificity is lower and return to Dr. Hoffman's point this morning that the observation of a higher proportion of soluble polymer may merely reflect the lower molecular weight (and hence greater solubility) of the polymer formed. A further point is that $TiCl_3$ catalysts may be prepared with greater or lesser cohesion; the polymer formed from these catalysts can duplicate their

physical structure and thus it is possible to obtain insoluble polymer containing varying proportions of trapped soluble polymer. This too is a process which can be affected by the presence or absence of hydrogen.

A. Schindler: (*1*) The solubility of ethylene in *n*-heptane at 40° was determined and found to be 0.159 millimols/liter Torr. The solubility of nitrogen was not determined since this value is too low for a simple experimental set-up. The rate of polymerization is proportional to the concentration of active catalyst sites occupied by adsorbed ethylene, whereby this concentration can be expressed by the partial pressure of ethylene in the gas phase or by the concentration of ethylene dissolved in the diluent. Since both expressions can be assumed to be strictly proportional inside the pressure range investigated, only a change in the numerical values of the constants involved in the kinetic derivations will result.

(*2*) The decrease in stereospecificity of polypropylene accompanying the addition of hydrogen during the polymerization was only quoted according to results reported by Natta. At the moment there exists no direct proof that the hydrogen on the β-carbon is involved in the formation of CHD-groups by an exchange reaction but an additional experimental result might be reported which also strongly supports this assumption.

In polymers, obtained with catalyst systems which yield rather high molecular weight polymers, only very small amounts of CHD-groups could be detected even at high deuterium concentrations in the feed. Since all of the most important reaction steps which terminate the growth of an individual polymer chain involve the hydrogen on the β-carbon, a high molecular weight polymer suggests a very low reactivity of this hydrogen under experimental conditions in agreement with its low exchange rate with deuterium. This result is in good agreement with the experiments reported by Drs. Hoffman, Fries, and Condit, where the authors used a catalyst system which yielded very high molecular weight polymers and therefore could not find inside the experimental error any tritium incorporated in the polymer other than by a chain transfer reaction.

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Nouveaux Composants des Catalyseurs de la Polymérisation de l'Ethylène dans des Conditions Habituelles et Inhabituelles

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Le but de la présente communication est l'examen de certains questions générales, sur le modèle de l'éthylène, concernant la dépendance du caractère de la polymérisation et des propriétés des polymères de la composition des composants organo-métalliques du catalyseur et de la méthode de leur obtention.

Les composants organo-lithiens (dont l'emploi pour la polymérisation a déjà été décrite par nous[1]) furent obtenus premièrement dans la série aliphatique; ce sont: l'éthyllithium, le *n*-butyllithium, le *n*-amyllithium, le *n*-dodécyllithium.

La préparation du catalyseur (type Ziegler) etait pareille dans tous les cas présentés ici: *n*-hexane saturé par l'éthylène, rapport de $RLiTiCl_4$ égal 1:1, mélange soigneux, température -65 à -70°C.

Pour les composants organo-lithiens ci-dessus mentionnés, l'absorption de l'éthylène se termine après 1 ou 1,5-heures avec rendement 3000–4000 g pour 1 équivg du composant organo-métallique.

L'absorption de l'éthylène se ralentit fortement (de dix fois) et le rendement diminue nettement (2,500 g) dans le cas où le composant organo-métallique initial n'est pas soluble dans l'hexane.

Les combinaisons organo-lithiennes aromatiques appartiennent toutes à ce type. Elles s'obtiennent toutes de même facon suivant une réaction d'échange entre aryl haloïde et alkyllithium. Dans les cas d'*o*-, *m*- et *p*-tolyllithium, *p*-bromphényllithium et *p*-chlorphényllithium l'échange était toujours effectué dans l'hexane ou le benzène à l'aide d'éthyllithium ou de butyllithium. L'aryllithium déposé était toujours soigneusement lavé par l'isopentane des traces d'alkyllithium, séché dens le vide, puis analysé. (Les variations en quantité du bromure de lithium ordinairement additionné n'influençaient en rien les paramètres du processus ultérieur.)

L'aryllithium solide insoluble était en suspension dans le *n*-hexane et il y était ajouté du tétrachlorure de titane soluble dans le *n*-hexane.

Convient-il d'attribuer le brusque ralentissement du processus de polymérisation à ce que dans un cas l'aryl est lié avec le lithium, alors que

dans l'autre cas c'est l'alkyl? Ou bien cela peut dépendre aussi de l'état physique, par exemple de la dispersibilité du composant organo-métallique.

La réponse à cette question peut en une certaine mesure être donnée par les expériences pratiquées avec le même aryllithium (précisément le phényllithium), cependant obtenu dans des conditions différentes de formation de la phase solide du composant.

Dans les conditions d'une capacité extreme de réaction des combinaisons organo-métalliques de lithium il est difficile de déterminer précisément le degré de dispersibilité. C'est pourquoi on a été obligé de se limiter à une appreciation visuelle au microscope.

Le phényllithium I (depuis le bromobenzène et le *n*-butyllithium dans l'hexane) est une poudre cristalline fine et légère. Le catalyseur type Ziegler était préparé de ce phényllithium comme ordinairement (voir ci-dessus). Début de la polymérisation à −15°C, activité maxima de 0–30°C rendement 2500 g pour 1 équiv-g du composant organo-métallique, le polymère a l'aspect d'une poudre. Le phényllithium II, (depuis le *n*-butyllithium dans le benzène) est un peu plus structuré. Le cours de la polymérisation est analogue. Le rendement est abaissé jusqu'a 1700 g. Le polymère est semblable à des granulations. Le phényllithium III (depuis l'éthyllithium dans le *n*-hexane) consiste en cristaux durs mais fins. La polymérisation est caractérisée par son début à +10°C, activité maxima à 25–30°C, petit rendement (480 g), polymère sous forme de poudre. Le phényllithium IV (depuis l'éthyllithium dans le benzène). Ce cas, du point de vue du rendement et d'autres paramètres du processus se différencie peu du précédent; cependant il est intéressant au point de vue de la forme extérieure du composant organo-lithien et du polymère obtenu avec sa participation. Le faut s'arrêter particulièrement sur ce cas.

Le phényllithium consiste en cristaux aculéiformes longs de 2–3 mm agrégés parallelement. Les polymères en granules sont composés pra une grande quantité de petits fils parallèles dont l'épaisseur est de l'ordre de 100–200 μ et la longueur de 1–3 mm. Les granules ont ainsi une dimension de 1,5–3 mm de diamètre et une longueur de 1–3 mm. Mécaniquement les granules peuvent etre divisées en petits fils séparés les composant. Puis, lors de l'examen de ces petits fils au microscope il se precise qu'ils sont formés de pseudo-cristaux allongés assez grands, d'une grandeur moyenne de 10–20 μ sur 150–200 μ, qui donnent une nette opacité dans la lumière polarisée et sont légèrement tordus en forme de spirale. L'angle de torsion n'est pas caractéristique, bien qu'il atteigne parfois 90 à 135°C. Ces formations sont à leur tour constituées comme de petites briques, des mêmes pseudo-cristaux, mais dix fois moindres. Ces derniers, d'une longueur de l'ordre de 10–20 μ furent aussi trouvés dans des échantillons de polyéthylène obtenus avec tous les catalyseurs phényllithium.

Ainsi les formations polymères reflètent en une certaine mesure les cristalites non solubles du composant organo-métallique du catalyseur.

Lors de la cristallisation depuis les formations en solution ou en fusion,

les structures de tous les polymères phényllithium vus au microscope ne se différencient presque pas et donnent des sphérulithes de caractère semblable.

Le poids moléculaire (250,000–300,000) et les propiétés mécaniques des polymères obtenus au moyen des catalyseurs phényllithuim se différencient peu les uns des sutres.

De nombreuses recherches effectuées par ailleurs sur des combinaisons organo-zinc et organo-cadmium permettent de tirer les conclusions suivantes: pour la série aliphatique caractéristiques sont les températures bases de début de la polymérisation, −70 à −75°C pour $(C_2H_5)_2Zn$; −50 à 60°C pour C_2H_5Li; −10 à −15°C pour $(C_2H_5)_2Cd$. Cette particularité varie peu si nous prenons un autre radical aliphatique (n-C_3H_7, n-C_4H_9). Les rendements sont ici de 3000–4000 g pour 1 équiv-g du composant organo-métallique.

Pour les combinaisons aromatiques du zinc et du cadmium qui sont insolubles dans l'hexane il se confirme ce qui a été dit pour le lithium: comparativement avec les combinaisons aliphatiques correspondantes la température du début du processus est plus élevée, la vitesse de l'absorption de l'éthylène et les rendements sont plus bas.

Il faut noter encore deux particularités: (*1*) les complexes du diarylcadmium avec le dioxane ne se différencient pas pour l'activite du diarylcadmium comme tel (conséquemment la présence de dioxane n'empêche pas la polymérisation); (*2*) pour les types de combinaisons obtenues pas nous[2,3] RCdX et RZnX (X est un haloïde), il est caractéristique un rendement à peu pres deux fois moindre que pour R_2Cd et R_2Zn (dépendance du nombre des radicaux utilisés). Et en général la polymérisation pour le type RMeX s'effectue plus faiblement.

Sur la base du matériel analysé on peut dire que: (*a*) le processus de polymérisation dépend non seulement du caractère chimique (C'est-à-dire métaux différents, radicaux différents), mais aussi de l'état physique du composant organo-métallique (et par cela même du catalyseur); (*b*) les propriétés mécaniques du polymère dépendent seulement de la composition chimique.

Il est aussi intéressant de noter, tout au moins pour le cas examiné par nous, l'absence de solvant (n-hexane) lors de polymérisation sur p-di-n-propylzinc–tétrachlorure de titane ne se reflète pas sur le poids moléculaire (environ 300,000) et sur les propriétés mécaniques des échantillons de polymère. Cependant le rendement était considérablement plus bas que dans le cas du procédé de polymérisation dans le n-hexane.

Les expériences étaient effectuées dans les conditions suivantes: dans un cylindre en verre disposé horizontalement (capacité 1,3 litre, grandeur de la surface 1250 cm^2) et remplit préalablement par de l'éthylène, il entrait deux courants indépendants de l'éthylène. Chaque courant à part passait dans une cuvette spéciale munie d'un dispositif de dosage permettant l'introduction du di-n-propylzinc (point d'ébul. 140°C) et du tétrachlorure de titane (point d'ébul. 136°C). En passant à travers la cuvette les

courants d'éthylène entrainaient avec eux les vapeurs de chacun des composants du catalyseur. Immédiatement après leur entrée dans le corps du cylindre, c'est-à-dire au moment de leur contact et de la formation de la phase solide du catalyseur, ils sont soumis à un mélange mécanique intense. Aussitôt le dépot du polymère commence sur les parois du récipient. L'absorption de l'éthylène n'est pas grande. Elle atteint seulement 10 litres par heure. Le rendement est de 1200 g pour 1 équiv-g du composant organo-métallique, c'est-à-dire de 2–2,5 fois plus bas qu'avec le procede de polymerisation dans le *n*-hexane avec le di-*n*-propylzinc dans les conditions ordinaires.

Le composant organo-métallique dont le radical non seulement se joindrait à la fin de la chaine polymère, mais aussi pourrait entrer dans la composition de la chaîne même, présentait aussi pour nous un certain intérêt.

Nous avons synthetisé du *p*-lithiumisopropenylbenzène contenant dans sa molécule en plus du lithium aussi une liaison double active. Il était obtenu par réaction d'échange entre le *p*-bromisopropénylbenzène et le *n*-butyllithium dans un milieu *n*-hexane. Vingt heures après le versement le depôt etait filtré, soigneusement lavé par *n*-hexane et isopentane des traces possibles de *n*-butyllithium, puis séché dans le vide. L'analyse de la poudre blanche finement cristalline obtenue a montré que nous avons du *p*-lithiumisopropénylbenzène contenant un mélange de bromure de lithium (environ 10%) ordinaire lors de réactions d'échange.

La combinaison obtenue de cette facon était prise comme composant du catalyseur type Ziegler pour la polymérisation de l'éthylène. La préparation du catalyseur et la polymérisation étaient effectuées dans un milieu de *n*-octane pur (chauffé préalablement dans un courant d'éthylène jusqu'a 90°). Rapport $RLi/TiCl_4$ ordinaire 1:1, température de mélange des composants 15°. Le catalyseur est coloré vivement en un rouge foncé particulier avec nuance de brun. La polymérisation de l'éthylène se produit à température de 20–60°C, sans dépendance marquée de la vitesse de l'absorption de l'éthylène de la température du milieu de réaction. La vitesse de l'absorption d'éthylene est assez petite.

Le processus de polymérisation durait 5 heures. Le rendement du polymère pur sec atteint 420 g par mole-g de *p*-lithiumisopropénylbenzène.

L'étude des spectres infra-rouges montre qu'à la différence du spectre infra-rouge du *p*-isopropényllithium initial, dans le polymère obtenuu ne liaison double n'est pas découverte. D'autre part, de grandes quantités de noyaux benzol et de combinaisons type RC_6H_4R sont présentes. Cela indique la croissance de la chaine polyéthylène au point de liaison lithium-carbone, ainsi que l'entrée du noyau gras-aromatique dans la chaîne principale au compte de la découverte d'une liaison double isopropényl. Le polymère obtenu donne les indices suivants de solidite: à 20°C. 265 kg/cm², allongement 460%; à 60°C, 275 kg/cm², allongement 1300%; à 100°C, 170 kg/cm², allongement 1800%. Les épreuves étaient effectuées sur dynamomètre avec temperature maintenue constante et vitesse d'allongement 30 mm par minute.

Conclusions

Il a été étudié sur un grand nombre de combinaisons organo-métalliques la dépendance des paramètres de la réaction de polymérisation et des propriétés du polymère obtenu de l'état physique (dispersibilite) du composant organo-métallique et de sa composition chimique; et il a été montré que le cours de la polymérisation dépend et du premier et du second facteur. Cependant les propriétés mécaniques du polymère dépendent seulement de la composition chimique du composant organo-métallique (caractère des radicaux, du métal, présence d'une liaison double active dans le composant organo-métallique).

Références

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Résumé

Les catalyseurs utilisés pour la polymérisation de l'éthylène peuvent, selon la méthode utilisée pour leur synthèse, se présenter sous des états différents par leur forme cristalline et leurs degrés de dispersion ou d'association. On a étudié à ce point de vue les composés organo-lithiens obtenus dans divers milieux (hexane, benzène ou éther), et par différents procédés. Leur mélange avec le tétrachlorure de titane a également été effectué dans des conditions variées. D'autre part, on a examiné systématiquement l'influence de la constitution chimique d'une cinquantaine de composé organo-métalliques du lithium, du cadmium et du zinc, utilisés comme catalyseurs, sur le déroulement de la polymérisation et sur les propriétés des polymères obtenus. Enfin, une polymérisation a été effectuée dans des conditions inhabituelles, en introduisant dans un courant d'éthylène des vapeurs de di-*n*-propylzinc et de tétrachlorure de titane. Les propriétés mécaniques du polyéthylène obtenu par ce procédé sont apparues identiques à celles du produit fabriqué avec le di-*n*-propylzinc en présence d'hexane. L'ensemble de ces résultats a permis de relier le déroulement de la polymérisation à la composition chimique du catalyseur et à l'état sous lequel se présente le constituant organo-métallique. Ainsi la structure du polymère—donc ses propriétés mécaniques—dépend de la seule composition chimique de ce constituant, et non pas de l'état physique sous lequel il se présente. Le catalyseur mixte, dans lequel le constituant organo-métallique est un organo-lithien renfermant une double liaison réactive apparait comme un catalyseur spécifique nouveau. Son emploi entraîne des particularités dans le processus de polymérisation et les propriétés du polymère obtenu diffèrent légèrement de celles du produit classique. Des études systématiques nous ont permis de mieux préciser l'influence du catalyseur sur l'existence de certains arrangements structuraux qui apparaissent lors de la formation du polyéthylène, et ne subsistent pas après sa fusion ou sa mise en solution, ainsi que sur la formation d'états d'organisations dits "secondaires" qui exercent une influence marqués sur les propriétés mécaniques du polymère obtenu.

Synopsis

The catalysts used for the polymerization of ethylene depending the method used for their synthesis can differ by their crystalline state and their degree of dispersion or association. Organolithium compounds prepared in various medium (hexane, benzene,

or ether) and by different procedures have been examined. Their mixture with titanium tetrachloride has also been carried out in various conditions. From the other side, the influence of the chemical constitution of 50 lithium, cadmium and zinc organometallic compounds used as catalysts has been examined in relation with the course of polymerization and the properties of the polymers. Finally, a polymerization was carried out in unusual conditions, by introducing in the ethylene stream vapors of di-*n* propyl-zinc and titanium tetrachloride. The mechanical properties of this polyethylene were identical with those obtained with di-*n*-propylzinc in the presence of hexane. All these results show a correlation between the course of the polymerization, the chemical composition of the catalyst and the state in which the organo-metallic compound is present. Consequently the structure of the polymer, as well as their mechanical properties, depends only on the chemical composition of this component, and not from its physical state. The mixed catalyst, when the organo-metallic component is a organolithium containing reactive double bonds, behaves as a new specific catalyst. Its use supposes some pecularities in the polymerization procedure; the properties of the polymer are a little different from those of the usual product. Systematic studies take in evidence the influence of the catalyst on the existence of some structural features which appear during the formation of the polyethylene, and disappear after melting or dissolution of the polymer, as well as on the formation of some secondary organized regions which influence markedly the mechanical properties of the polymer.

Zusammenfassung

Die zur Äthylenpolymerisation verwendeten Katalysatoren können je nach dem zu ihrer Darstellung verwendeten Verfahren in verschiedenen Formen bezüglich ihres Kristallzustandes und ihres Dispersions- oder Assoziationsgrades auftreten. Von diesem Gesichtspunkt aus wurden die in verschiedenen Medien (Hexan, Benzol oder Äther) und durch verschiedene Verfahren gewonnenen Organolithiumverbindungen untersucht. Auch ihre Mischung mit Titantetrachlorid wurde unter verschiedenen Bedingungen durchgeführt. Ändrerseits wurde systematisch der Einfluss der chemischen Konstitution von etwa fünfzig als Katalysatoren verwendeten organometallischen Verbindungen von Lithium, Kadmium und Zink auf den Ablauf der Polymerisation und auf die Eigenschaften der erhaltenen Polymeren untersucht. Schliesslich wurde eine Polymerisation unter ungewöhnlichen Bedingungen, indem in einen Äthylenstrom Di-*n*-propylzinkund Titanteträchloriddämpfe eingeführt wurden, erreicht. Die mechanischen Eigenschaften des so erhaltenen Polyäthylens waren mit denjenigen des in Gegenwart von Hexan mit Di-*n*-propylzink hergestellten Produktes identisch. Die Gesamtheit der erhaltenen Ergebnisse ermöglichte es, den Polymerisationsverlauf zu der chemischen Zusammensetzung des Katalysators und zum Zustand der organometallischen Komponente in Beziehung zu bringen. So hängt die Struktur des Polymeren und damit seine mechanischen Eigenschaften nur von der chemische Zusammensetzung dieser Komponente ab und nicht vom physikalischen Zustand, in welchem sie auftritt. Der Mischkatalysator, dessen organometallische Komponente eine Organolithiumverbindung mit einer reaktionsfähigen Doppelbindung ist, erscheint als neuartiger, spezifischer Katalysator. Seine Verwendung führt in den Polymerisationsprozess Besonderheiten ein und die Eigenschaften des erhaltenen Polymeren unterscheiden sich etwas von denjenigen des klassischen Produktes. Systematische Untersuchungen haben eine bessere Festlegung des Katalysatoreinflusses auf das Vorhandensein gewisser bei der Bildung des Polyäthylens auftretender aber bei seinem Schmelzen oder in-Lösung-Gehen verschwindender Strukturen sowie auf die Bildung organisierter, "sekundär" genannter Zustände, die einen merklichen Einfluss auf die mechanischen Eigenschaften des erhaltenen Polymeren besitzen, ermöglicht.

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Étude du Rôle de l'Hydrogène dans la Polymérisation du Propylène par l'Emploi d'Hydrogène Marqué au Tritium

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1. Introduction

La plupart des systèmes catalytiques stéréospécifiques utilisés pour la polymérisation du propylène ont tendance à donner des molécules de polypropylène de poids moléculaire très élevé. Or, l'utilisation du polymère est étroitement liée à ses propriétés d'écoulement à l'état fondu, donc au poids moléculaire.

Pour régler le poids moléculaire, il a été proposé d'effectuer la polymérisation en présence d'hydrogène qui a la propriété de provoquer une réaction de terminaison de chaînes. Un mécanisme de cette action de l'hydrogène a été donné par Natta, Mazzanti, Longi, et Bernardini.[1]

Il nous a paru intéressant de connaître quelle pouvait être la fraction de l'hydrogène mis en oeuvre qui intervient dans cette réaction de terminaison de chaînes. Des analyses, au cours de diverses expériences, avaient auparavant montré que 60–65% de cet hydrogène étaient consommés et qu'une partie de cet hydrogène consommé intervenait dans une réaction secondaire: l'hydrogénation du propylène en propane.

Comme les quantités d'hydrogène introduites à la polymérisation sont extrêmement faibles, comparées aux autres réactifs (propylène en particulier), les méthodes d'analyse classique ne permettent pas d'obtenir des résultats interprétables.

Nous avons donc fait appel aux méthodes des traceurs radioactifs et procédé à des expériences de polymérisation du propylène en présence d'hydrogène marqué au tritium.

Diverses mesures de radioactivité ont permis de vérifier les hypothèses de départ et de fixer avec une précision satisfaisante les proportions d'hydrogène intervenant dans les réactions de terminaison des chaînes et d'hydrogénation du propylène en propane.

2. Polymérisation du Propylène en Présence d'Hydrogène Tritié

Les expériences ont été conduites dans une installation pilote de polymérisation continue, capable de produire 3 kg à l'heure de polypropylène.

Le catalyseur utilisé possède une stéréospécificité élevée. (Il est du type de ceux décrits dans un brevet de Eastman Kodak.[2])

L'hydrogène est introduit sous forme dissoute dans le monomère alimentant le réacteur. Un dispositif permet d'assurer une grande constance de sa concentration qui pendant l'expérience décrite a été de 65 p.p.m. (en poids par rapport au monomère).

L'alimentation en monomère a été de 6 kg à l'heure, les conditions étant fixées de telle sorte que environ 50% du monomère soient polymérisés en polypropylène.

La quantité d'hydrogène introduite a donc été de 0,4 g par heure. La concentration en tritium dans cet hydrogène, correspond à 6,4 mCuries pour 100 g d'hydrogène.

A la sortie du réacteur, on sépare le polymère; on récupère le monomère non polymérisé dont on sépare l'hydrogène qui n'a pas réagi.

On a vérifié, par analyse chromatographique, que 60% de l'hydrogène introduit avec le monomère avaient disparu.

Les mesures de radioactivité sur le monomère récupéré ont permis de conclure que les $^2/_3$ de l'hydrogène combiné avaient hydrogéné le propylène en propane, l'autre tiers avait servi à limiter le poids moléculaire du polymère dont la viscosité inhérente est de 174 cm^3/g, mesurée à 130°C sur une solution dont la concentration est égale à 0,2% dans la tétraline à 20°C.

3. Étude du Polymère

Le polymère est fractionné par une précipitation sélective, suivie d'une dissolution sélective, effectuées dans une colonne remplie d'un support inerte.

Trois fractionnements identiques sont effectués, en mettant en oeuvre 3 g de polymère dans chaque opération. Les espèces de viscosités identiques ou très voisines obtenues dans ces trois opérations sont réunies en dix fractions. Cette réunion est nécessaire pour obtenir une prise d'essai suffisante pour le dosage radiochimique.

La courbe de répartition intégrale correspondante est identique à celle obtenue à partir d'un fractionnement unique en quinze fractions.

Les fractions sont caractérisées par leurs viscosités inhérentes mesurées dans la tétraline à 130°C (concentration de 0,2% à 20°C). Leurs masses moléculaires moyennes en poids sont calculées par la relation:

$$\eta_{inh} = 3{,}21 \times 10^{-3} M^{0.88}$$

où la concentration est exprimée en g/cm^3.

Nous avons établi cette relation par la mesure en diffusion de la lumière, des masses moléculaires moyennes en poids de fractions de viscosités connues. Ces mesures ont été effectuées dans l'α-chloronaphthalène à 135°C, avec un photogoniodiffusiomètre SOFICA. L'étalonnage a porté sur treize fractions, obtenues à partir de polypropylène de même type que celui

étudié ici et suivant le même procédé de fractionnement. L'échelle des masses moléculaires ainsi couverte s'étend de 25.000 à 1.000.000.

Les résultats du fractionnement figurent dans le Tableau I, où les cinq premières colonnes indiquent respectivement le numéro des fractions, leur pourcentage, les pourcentages cumulatifs et leur masse moléculaire $\bar{M}_w$.

TABLEAU I

N°	%	I(pi)	η_{inh}	$\bar{M}_w \times 10^{-3}$	$\bar{M}_n \times 10^{-3}$	Hydrogène, p.p.m. Théorique	Hydrogène, p.p.m. Trouvé	Atome d'hydrogène par molécule
1	14,04	7,02	21,9	22	11	91	100	1,1
2	19,68	23,88	42,2	46	<46	>21	28,2	—
3	5,60	36,52	64,2	75	75	13,3	14	1,05
4	6,13	42,38	81,3	95	95	10,5	8,3	0,79
5	5,05	47,97	92	110	110	9,1	10,4	1,14
6	8,88	54,94	110	135	135	7,4	6	0,81
7	9,30	64,03	151,5	195	195	5,1	6,3	1,23
8	10,32	73,79	212	275	275	3,6	4	1,10
9	11,36	84,58	264	370	< 370	> 2,7	2	—
10	9,74	95,13	633	1.000	<1.000	> 1	2,2	—

4. Dosage de Radioactivité

Le tritium est dosé par scintillation en milieu liquide avec un appareil Lie-Belin type Carbotrimètre.

Les prises d'essais sont brûlées dans un tube de Groote pour les échantillons gazeux et dans une bombe, sous 25 bars d'oxygène, pour les échantillons solides pastillés. L'eau formée quantitativement est incorporée dans un mélange scintillant eau–éthanol–toluène contenant 4 g/l PPO et 0,1 g/l POPOP. Le ternaire est placé dans une cuve en quartz vue par deux photomultiplicateurs montés en coïncidence, l'ensemble étant protégé par 5 cm de plomb et réfrigéré à -12°C.

Dans ces conditions, pour une haute tension de 1.300 V et une bande passante d'impulsions de 3–50 V, le rendement de détection du tritium atteint 6%. On décèle 2 cpm soit une sensibilité d'environ $1,5 \times 10^{-11}$ Curie.

L'activité spécifique de l'hydrogène a été calculée de façon que les sensibilités limites des méthodes physiques et radiochimiques soient atteintes pour des poids moléculaires identiques. La grande sensibilité du Carbotrimètre a ainsi permis d'opérer sur une activité totale de tritium extrêmement faible eu égards aux quantités de produits mises en jeu, ce qui a rendu négligeable tout problème de sécurité.

5. Interprétation des Résultats

Il est intéressant de connaître le nombre d'hydrogène fixé par molécule. Il faut donc comparer la masse moyenne en nombre, $\bar{M}_n$, de chaque frac-

tion, avec la teneur en hydrogène fixé. Les masses connues des fractions sont des masses moyennes en poids $\bar{M}_w$. On peut confondre approximativement $\bar{M}_n$ et $\bar{M}_w$ pour des fractions étroites, ce qui est le cas des fractions 3, 4, 5, 6, 7, 8.

Cette approximation n'est plus légitime pour les fractions 1 et 2. La masse moléculaire moyenne en nombre de la fraction 1 a été déterminée directement par ébulliométrie. Pour la fraction 2, l'ébulliométrie n'est pas suffisamment précise. Tout ce que nous pouvons dire, c'est que la masse $\bar{M}_n$ est inférieure à $\bar{M}_w$.

Les masses $\bar{M}_n$ des fractions 9 et 10 sont inaccessibles à une mesure directe précise et sont d'ailleurs sans intérêt, étant donné la trop faible précision du dosage radioactif.

Connaissant les masses moléculaires $\bar{M}_n$, nous calculons la teneur théorique en hydrogène, en supposant qu'un atome se soit fixé par molécule, pour provoquer la terminaison des chaînes.

Les résultats obtenus sont portés dans le Tableau I. Dans la colonne 7, figurent les proportions d'hydrogène théorique exprimées en p.p.m.; dans la colonne 8, figurent les proportions d'hydrogène trouvées par dosage radioactif; cette proportion est exprimée en nombre d'atomes par molécule dans la colonne 9.

La moyenne arithmétique des résultats donnés dans la colonne 9 est égale à 1,03, valeur très proche de la valeur théorique. Ces résultats expérimentaux confirment donc qu'il y a fixation d'un atome d'hydrogène par molécule dans le mécanisme de terminaison des chaînes.

Conclusion

Le mécanisme de terminaison des chaînes macromoléculaires par l'hydrogène au cours de la polymérisation stéréospécifique du propylène a fait l'objet d'un schéma théorique proposé par Natta et collaborateurs. Nous avons vérifié expérimentalement ce schéma grâce à la grande sensibilité des méthodes radiochimiques. L'emploi du tritium traceur d'hydrogène, conjugué avec une méthode originale de fractionnement, a permis de vérifier que, dans un régime continu de polymérisation, il y a fixation statistique d'un seul atome d'hydrogène par macromolécule.

Références

1. Natta, Q., G. Mazzanti, P. Longi, et F. Bernardini, *Chim. Ind.* (*Milan*), **41**, 519 (1959).

2. Eastman Kodak Co., Brevet Français 1.228.410.

Résumé

Le propylène a été polymérisé, selon un procédé continu, au moyen d'un catalyseur stéréospécifique, en présence d'hydrogène marqué au tritium. Les dosages d'hydrogène en amont et en aval du réacteur ont montré qu'environ 60% de cet hydrogène avaient été consommés durant la polymérisation. Le polypropylène fabriqué est radioactif. Il a été fractionné et la mesure de la radioactivité de chacune de ces fractions, dont le poids moléculaire a été déterminé par ailleurs, montre qu'un seul atome d'hydrogène a

été fixé sur chaque macromolécule. La radioactivité mesurée sur le propylène non polymérisé montre que de l'hydrogène a également été fixé sur le propylène pour former du propane.

Synopsis

Propylene has been polymerized, in a continuous procedure, with a stereospecific catalyst, containing tritiated hydrogen. The determination of hydrogen downwards and upwards inside of the reactor show that about 60% of the hydrogen was consumed during the polymerization. The polypropylene was radioactive. After fractionation, the radioactivity and the molecular weight of each fraction have been determined; each molecule contains one hydrogen atom. The radioactivity of the propylene-monomer shows also that some hydrogen is fixed on the propylene giving some propane.

Zusammenfassung

Propylen wurde nach einem kontinuierlichen Verfahren mit einem stereospecifischen Katalysator in Gegenwart von mit Tritium markiertem Wasserstoff polymerisiert. Wasserstoffbestimmung vor und nach dem Reaktor zeigten, das 60% des Wasserstoff während der Polymerisation verbraucht werden. Das gebildete Polypropylen ist radioaktiv. Es wurde fraktioniert und die Messung der Radioaktivität der Fraktionen, deren Molekulargewicht ebenfalls bestimmt wurde, zeigte, dass pro Makromolekül ein Wasserstoffatom gebunden wurde. Die am nicht polymerisierten Propylen gemessene Radioaktivität zeigt, dass Wasserstoff auch von Propylen unter Bildung von Propan gebunden wird.

Discussion

A. S. Hoffman (*California Research Corp., Richmond, Calif.*): Have you considered the possibility that after a growing chain has been terminated by tritium, the reinitiation of a new chain at this same catalyst site could also incorporate tritium into the polymer?

A. Perez: La valeur expérimentale trouvée pour la quantité d'hydrogène tritié fixée sur la chaîne macromoléculaire (1 atome d'H/chaîne macromoléculaire) laisse supposer que la réaction

$$\underset{\text{Cat H}}{(+)(-)} + CH_2{=}CH{-}CH_3 \rightarrow \underset{\text{Cat } CH_2{-}CH_2{-}CH_3}{(+)(-)}$$

ne se produit pas dans les conditions expérimentales que nous avons observées pour l'essai.

Rocaboy: (*1*) Les résultats que vous avez indiques (1 atome H marqué) ne sont-ils pas faussés par des réactions de transfert avec le catalyseur d'une part, par des réactions de substitution sur le polymère formé (effet isotopique) d'autre part? (*2*) Quelle est la sensibilité de la méthode g tritium/g de polymère?

G. Bourat: (*1*) Nous avons considéré l'effet isotopique comme a priori très faible mais nous ne l'avons pas vérifié expérimentalement. (*2*) Avec l'activité spécifique utilisée la sensibilité limite atteignait 2 ppm H_2. La précision est de l'ordre de 50% sur les fractions de hauts poids moléculaires f9, f10; de 10% pour les autres fractions.

I. Pasquon (*Italie*): Nous avons observé que le poids moléculaire du polypropylène que l'on obtient en présence de H_2 dépend d'une façon très sensible du type de composé organométallique d'aluminium utilisé (par exemple $Al(C_2H_5)_3$ et $Al(C_2H_5)_2Cl$). Avez-vous des données semblables et pouvez vous avancer des hypothèses pour justifier ces résultats?

A. Perez: Le seul système catalytique utilisé a été $AlCl_2C_2H_5$-$PO[N(CH_3)_2]_3$-$TiCl_3$ L'étude de la réaction de transfert avec H_2 tritié en présence d'autres systèmes catalytiques n'a pas été étudiée.

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The Role of Hydrogen in Ziegler-Natta Polymerizations

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It is well known that hydrogen gas can be used to lower and to control the molecular weight of polyolefins made by Ziegler-Natta type polymerizations.[1,2] Natta and co-workers[2] have postulated a mechanism in which hydrogenation of a catalyst–growing chain bond occurs, yielding a catalyst hydride site and a dead chain with a hydrogen atom incorporated at the end.

$$[\text{Cat}]^+\,\bar{\text{C}}\text{H}_2\text{—CH(CH}_3\text{)—P} \xrightarrow{\text{H}_2} [\text{Cat}]^+\,\bar{\text{H}} + \text{CH}_3\text{CH(CH}_3\text{)—P}$$

where P is polymer. Furthermore, the catalyst hydride site may then be alkylated by the olefin monomer, initiating the growth of a new polymer chain:

$$[\text{Cat}]^+\,\bar{\text{H}} \xrightarrow{\text{CH}_2\text{=CH(CH}_3\text{)}} [\text{Cat}]^+\,\bar{\text{C}}\text{H}_2\text{—CH}_2\text{—CH(CH}_3\text{)} \xrightarrow{\text{CH}_2\text{=CH(CH}_3\text{)}} \text{etc.}$$

We have investigated this mechanism by the use of tritium as a tracer for the hydrogen. Polymer chains initiated by the catalyst hydride site and terminated by hydrogen should contain two tritium-labeled chain ends. Any other mechanism of initiation and/or termination could lead to only one or even no tagged chain ends per molecule.

Polymerizations were run with $TiCl_3$–$AlEt_2X$ catalysts (where X is Cl or I) under conventional conditions in the presence of hydrogen gas to which tritium had been added as a tracer. Polymer fractions were assayed for tritium content, and the measured radioactivities were applied to the calculation of molecular weights which were then related to the intrinsic viscosities of the fractions. Details are given in the experimental part.

Two monomers were studied, propylene and 4-methyl-1-pentene. Previous work has shown that these monomers behave similarly towards Ziegler-Natta catalysts, and both show a marked reduction in polymer molecular weight when polymerization is conducted in the presence of hydrogen.[3]

4-Methyl-1-pentene was used in most of the work, particularly where an accurate accounting for tritium was required. This monomer can be polymerized at atmospheric pressure, which minimizes complications due to leakage from the reaction system. Propylene was used as a monomer in one experiment where the polymer was subsequently fractionated into narrow molecular weight fractions.

RESULTS AND DISCUSSION

Exchange Reactions and Isotope Effect

In order to use the tritium-labeling technique to study the mechanism by which hydrogen terminates polymer chains, it is necessary to establish that tritium is not incorporated into the polymer by extraneous exchange reactions with hydrogen either in the monomer before it is polymerized or in the polymer after it is formed.

A polymerization of 4-methyl-1-pentene was conducted under a tritium–hydrogen atmosphere to about 50% conversion, and a tritium material balance was obtained on the reaction system. These results are shown in Table I. It can be seen that a negligible amount of radioactivity is present in the recovered monomer at this stage of conversion and also that the specific activity of the polymer fractions increases as their solubility increases. Despite the high specific activity of the 2-methylpentane fraction, this hydrogenated form of the monomer represents less than 2% of the original monomer present. However, the hydrogen consumed by this

TABLE I
Material Balance of Tritium in Poly-4-methyl-1-pentene Polymerization[a]

Fraction	Total amount	Specific activity, disintegrations/sec./g. or cc. $\times 10^{-3}$	Total activity, disintegrations/sec. $\times 10^{-6}$	Portion of total used, %
Initial H_2 atmosphere	291 cc.	68	20	
Final H_2 atmosphere	242 cc.	68	17	
H_2 consumed	49 cc.	—	~3	
Heptane	237 cc.	0.34	0.081	2.6
4-Methyl-1-pentene	48 cc.	0.57	0.028	0.9
2-Methylpentane	1.7 cc.	1000	1.7	54.0
Quench solution-soluble polymer	0.48 g.	640	0.31	9.8
Hot heptane-soluble polymer	1.69 g.	351	0.59	18.7
Hot heptane-insoluble polymer	28.1 g.	15.4	0.43	13.6
Catalyst residue	2.96 g.	4.0	0.012	0.4
H_2 accounted for	—	—	~3.2	

[a] The accuracy of the results is probably within a range of ±10%.

side reaction was over 50% of the total. The overall tritium balance appears reasonable.

Attempts were made to exchange tritium with preformed poly-4-methyl-1-pentene under polymerization conditions but in the absence of monomer. The recovered polymer did not contain significant amounts of tritium. (See Experimental Section F.)

In order to use the tritium-labeling technique quantitatively, it is also necessary to know whether there is any difference in the rates of reaction of tritium and hydrogen, i.e., the kinetic isotope effect. This effect was measured by observing the rate of hydrogen consumption and the change in tritium concentration in the gas phase during a polymerization of 4-methyl-1-pentene. There was no measurable isotope effect in this reaction system. (See Experimental Section G.) Actually, three reactions involving hydrogen are occurring: hydrogenation of monomer and initiation and termination of polymer chains. If there were an isotope effect, one would expect tritium to react more slowly in all of these reactions; therefore, we feel it is safe to conclude that the isotope effect for chain initiation and termination is negligible.

Propylene Polymerization

To establish a relationship between tritium content and molecular weight, propylene was polymerized under labeled hydrogen and the polymer separated into narrow molecular weight fractions. Tritium contents and intrinsic viscosities were measured on the fractions. We selected for comparison the relationship of Kinsinger and Hughes[4] based on fractionated polypropylenes:

$$[\eta] = 1.38 \times 10^{-4}(\bar{M}_n)^{0.80} \quad (1)$$

where intrinsic viscosities were measured under the same conditions as ours, i.e., at 135°C. in decalin. The best agreement was achieved by assuming two labeled chain ends per molecule. These data are shown in Table II and Figure 1.

The agreement is excellent for the higher molecular weight fractions which comprise the bulk of the polymer. The agreement is progressively poorer as one goes to lower molecular weights. The lowest molecular weights measured by Kinsinger and Hughes were about 14,000, and it is in this range and below that our data deviate most seriously from their relationship.

In the lower molecular weight range our values differ from Kinsinger and Hughes by roughly a factor of 2. Assuming that their relationship is still valid at the lower molecular weights, our values would indicate that in this range the average molecule contains only one tagged chain end. The lower molecular weight fractions of polypropylene are considered to be less stereoregular than the higher fractions,[5] and they are therefore presumably produced by a different mechanism. The mechanism which produces the lower molecular weights may be one which gives only one tagged

TABLE II
Molecular Weights and Intrinsic Viscosities of Tritium-Labeled Polypropylene Fractions

Fraction	Weight, mg.	Integral weight, %	$[\eta]$, dl./g.	Activity, disintegrations sec.-mg.	$\bar{M}_N \times 10^{-3}$ Calc.[a]	$\bar{M}_N \times 10^{-3}$ Pred.[b]	$[(\bar{M}_N)$ Calc.$]/[(\bar{M}_N)$ Pred.$]$
3	42.6	1.8	0.08	1560	4.5	2.8	1.60
4	96.3	5.8	0.15	560	12.6	6.2	2.03
5	61.3	8.3	0.19	430	16.5	8.3	1.98
6	50.2	10.4	0.23	320	22.1	10.6	2.08
8	103.2	14.7	0.36	320	22.1	18.6	1.19
9	110.4	19.3	0.43	190	37.2	23.3	1.60
10	153.8	25.7	0.54	170	41.6	30.8	1.35
11	232.7	35.3	0.80	125	56.7	50.5	1.12
12	115.1	40.0	0.96	82	86.5	63.0	1.37
13	144.5	46.1	1.30	75	94.4	92.3	1.02
14	487.3	66.5	2.18	43	165.0	176.0	0.94
15	425.5	84.3	3.50	24	295.0	340.0	0.87
16	191.5	92.0	3.20	26	272.0	287.0	0.95
17	112.5	96.8	3.30	24	295.0	296.0	1.00
18	40.4	100.0	2.85	29	244.0	246.0	0.99
Crude polymer	—		1.90	256	27.6	149.0	0.19

[a] Based on two tritium-labeled hydrogens per macromolecule.
[b] Predicted from $[\eta] = 1.38 \times 10^{-4} (\bar{M}_n)^{0.80}$.

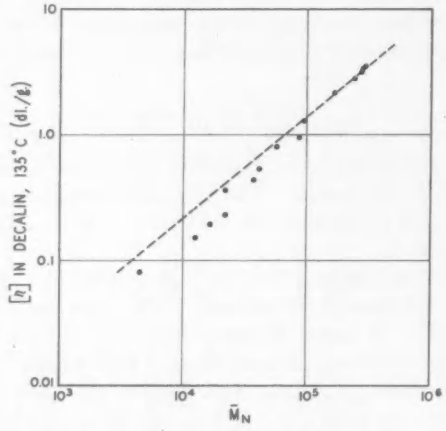

Fig. 1. Comparison of $[\eta]$–$\bar{M}_n$ relationships for fractionated polypropylenes: (●) $\bar{M}_n$ calculated from tritium end-labeling, assuming two tagged ends per molecule; (- -) relationship obtained by Kinsinger and Hughes[4] from osmotic pressure measurements.

chain end. It is also possible that there might have been some degradation of our polymer sample during workup and deposition on the elution column. Scission of molecules tagged at both ends would also give lower molecular weight polymer with only one tagged end.

The lack of agreement between the two methods of estimating molecular weight of the crude polymer (last line, Table II) is an indication that the molecular weight distribution is broad in the unfractionated material.

For the purposes of calculation, it was assumed that reaction with hydrogen is the only reaction by which growing chains are terminated. This is probably not rigorously true. However, this situation was approached as closely as feasible in our propylene polymerization by keeping the catalyst concentration relatively low and operating at room temperature, low propylene partial pressure (20 psig), and high hydrogen content (about 42 mole-%). Natta and co-workers[2,5,6] operated at conditions which were not as mild as ours and discounted all chain termination or transfer reactions except chain transfer with hydrogen and propylene monomer. Bier and co-workers[7] and Kohn and co-workers[8] show that essentially all polypropylene chains formed in the absence of hydrogen remain attached to catalyst sites until the polymerization is finally quenched. Termination by transfer with monomer must therefore also be unimportant.

We feel that the agreement between our tritium-calculated molecular weights and the osmometric molecular weights of Kinsinger and Hughes in the range of 40,000–300,000 is strong evidence that a hydrogen or tritium atom is incorporated at each end of the polymer molecule. It therefore lends support to Natta and co-workers' postulated mechanism. It also suggests that for the initiation of high molecular weight polymers the catalyst hydride site formed during the hydrogen termination step is more active than remaining catalyst alkyl sites.

4-Methyl-1-pentene Polymerizations

Isotactic poly-4-methyl-1-pentene is too insoluble to fractionate into narrow molecular weight cuts by the means used for polypropylene. The crude polymer does contain portions that are soluble in the cold quench solution and in hot heptane, and so a gross separation can be made. The fractions may differ in tacticity, but they also differ in molecular weight as measured by intrinsic viscosity.

If we assume on the basis of the polypropylene data that both chain ends of the average poly-4-methyl-1-pentene molecule are tritium-labeled, we can calculate molecular weights from the radioassays. We can then establish a relationship between number-average molecular weight and intrinsic viscosity. This relationship for poly-4-methyl-1-pentene is shown in Figure 2. It can be expressed by the equation:

$$[\eta] = 0.6 \times 10^{-4}(\bar{M})^{0.92} \tag{2}$$

where $[\eta]$ is measured in decalin at 135°C. Since these measurements were obtained on polymer samples which may have had a fairly broad molecular weight spread, the relationship is probably not as accurate as that obtained with fractionated polypropylene.

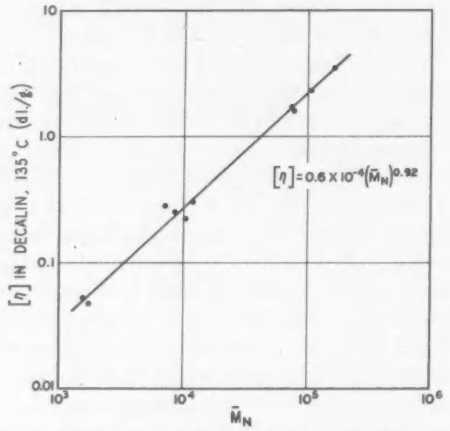

Fig. 2. Relationship between $[\eta]$ and $\bar{M}_n$ for poly-4-methyl-1-pentene calculated from tritium end-labeling, assuming two tagged ends per molecule.

EXPERIMENTAL

A. Materials

The 4-methyl-1-pentene was prepared by dimerization of propylene.[9] It was distilled, passed through a silica gel column, and stored over sodium wire and nitrogen. The propylene was obtained from the Mathieson Company and was CP grade. Phillips pure-grade *n*-heptane was employed as solvent in polymerizations and extractions. It was passed through a silica gel column and stored over sodium wire and nitrogen. The $TiCl_3$ was obtained from the Stauffer Chemical Company and is the violet α-$TiCl_3$-AA form. The aluminum alkyls were obtained from the Texas Alkyls Company and were used pure or diluted 50% with heptane.

B. Polymerization

1. Propylene. Propylene was polymerized at room temperature in a flask containing a small pressure-tight neoprene membrane through which the tritium tracer was added. The following procedure was used. A 100-ml. portion of *n*-heptane was added to the open flask blanketed with nitrogen. Then 0.286 g. of $TiCl_3$-AA was added, and shortly afterward 0.362 ml. of $AlEt_2Cl$ was syringed into the system. Stirring was accomplished with a magnetic stirrer. The flask was purged with hydrogen gas and sealed at 1 atm. pressure. Then 4 ml. of tritium tracer gas containing about 0.5 mc. was introduced through the membrane, and the system was pressured with propylene to 20 psig through a purged inlet line. The system was maintained at 20 psig for about 5 hr. After quenching the reaction and working up the polymer (see below), approximately 13.2 g. of crude polymer was recovered.

2. 4-Methyl-1-pentene. The 4-methyl-1-pentene polymerizations were also run in a flask sealed with a pressure-tight neoprene membrane. *n*-Heptane was employed as solvent with $TiCl_3/AlEt_2Cl$ and $TiCl_3/AlEt_2I$ catalyst systems. The order of addition was generally: heptane, $TiCl_3$, $AlEt_2X$, although in a few cases the aluminum alkyl was added before the $TiCl_3$. The results were apparently not affected by the order of addition of the catalyst components.

Catalyst–solvent mixtures were prepared under hydrogen atmospheres (or under nitrogen and later switched to hydrogen). After sealing the flask at 1 atm. pressure, 1 or 2 ml. of the tritium tracer in hydrogen was injected from a syringe through the self-sealing membrane. The flask was shaken, and the monomer was added at once from a syringe through the membrane.

The $TiCl_3$ concentrations varied from 0.0055 to 0.0166 moles Ti/l. and the Al/Ti mole ratio varied from 2.0 to 2.7. 4-Methyl-1-pentene concentrations ranged from 1.32 to 2.64 moles/l. The reactions were run at 25 or 50°C., usually from one to several hours. A sample of the vapor phase was taken before addition of the monomer in some cases. The data from six of the 4-methyl-1-pentene polymerizations are reported in detail in this paper.

C. Sampling and Fractionation

1. Propylene. After releasing the propylene pressure the reaction was quenched by mixing the slurry with an excess of methanol to which concentrated HCl had been added (25 ml. HCl/l. of alcohol). The slurry was stirred and then filtered; the crude polymer was washed several times in methanol and dried in a vacuum oven at 80°C. overnight.

The crude polypropylene was fractionated in an elution column after deposition on glass beads, a technique similar to that of Mendelson[10] being used. The solvent–nonsolvent mixture employed was *o*-dichlorobenzene–methyl carbitol to which 0.2% Ionol had been added as degradation inhibitor. The fractionation was conducted over nitrogen at ca. 172°C.; 22 cuts were taken between 10 and 100% *o*-dichlorobenzene. The intrinsic viscosities of the fractions were determined by duplicate measurements on a single sample at one concentration in decalin at 135°C. as the solvent. Extrapolation to zero concentration was made by use of the Mark-Houwink equation with a Huggins' constant of 0.42.[4] The tritium contents of the fractions were assayed.

2. 4-Methyl-1-pentene. At the end of the reaction the polymer slurry was mixed with an isopropanol or methanol quench solution as above and filtered at room temperature. The first filtrate was recovered and evaporated to dryness. This residue was extracted with heptane; the insoluble portion is called catalyst residue, and the soluble portion (polymer) is called quench solution-soluble. The crude polymer remaining after the first filtration step was washed in methanol and dried in a vacuum oven at 80°C. overnight. This dried crude polymer was extracted with refluxing hep-

tane; the hot heptane-soluble and hot heptane-insoluble portions were recovered.

In the case of the experiments where a tritium material balance was run, the polymer slurry was centrifuged before quenching and a sample of the liquid phase was obtained. This was separated by gas chromatography into heptane, 2-methylpentane, and 4-methyl-1-pentene portions. The polymer was worked up as before.

The intrinsic viscosities of the three polymer portions were determined in decalin at 135°C. in a manner similar to polypropylene. The tritium contents of each of the four portions (and of the heptane, 2-methylpentane, and 4-methyl-1-pentene) were then assayed.

D. Radioanalysis

All tritium measurements were made with a Tracerlab Model CE-1 liquid scintillation counter. Gas samples, catalyst residues, and hot heptane-soluble and heptane-insoluble polymer portions were combusted to water in a small CuO-filled furnace. The radioactive water produced was collected in a trap containing several milliliters of water, and a 1-ml. aliquot was countered in a scintillation phosphor recipe containing alcohol. Quench solution-soluble samples, heptane, 2-methylpentane, and 4-methyl-1-pentene were counted directly with the usual phosphor solutions. Absolute disintegration rates were obtained from the count rates by use of an internal standard.

E. Molecular Weight Calculation

The molecular weights were calculated from eq. (3)

$$\bar{M}_n = \left[\frac{\dfrac{\text{disintegrations/sec.}}{\text{g.-atom } H_2}}{\dfrac{\text{disintegrations/sec.}}{\text{g. of sample}}}\right]\left[\frac{\text{No. labeled chain ends}}{2}\right] \qquad (3)$$

In our calculations we use two for the number of labeled chain ends.

F. Exchange Experiments

In two experiments a nonradioactive poly-4-methyl-1-pentene sample was substituted for its monomer and stirred with the catalyst at 50°C. for several hours under a tritium-labeled hydrogen atmosphere. The polymer was recovered, washed, dried, and assayed for tritium content. In the first experiment a sample of crude polymer was used, and in the second experiment the same polymer after heptane extraction in a Soxhlet apparatus was used. The results are shown in Table III and are compared with two 4-methyl-1-pentene polymerizations conducted under essentially identical conditions.

TABLE III
Comparison of Polymerizations and Exchange Studies with Poly 4-methyl-1-pentene

	Specific activity, disintegrations/sec./mg.				
	Catalyst residue	Quench solution-soluble	Hot heptane-soluble	Hot heptane-insoluble	Crude polymer
Polymerizations	118	3800	552	85	185
	25	2250	340	47	--
Exchange with					
Crude polymer					0
Hot Heptane-insoluble polymer				<7	

G. Isotope Effect

The isotope effect was estimated in a polymerization of 4-methyl-1-pentene under a tritium-labeled atmosphere. The reaction was run in a three-necked 500-ml. flask, closed to the atmosphere but containing an attached vacuum bulb for periodically removing 2-ml. gas samples. The flask was water jacketed and kept at 25°C. under a nitrogen blanket. We then added, in the following order: 150 ml. heptane, 3.2 ml. of 50% $AlEt_2Cl$, 1 g. $TiCl_3$-AA, and 100 ml. of 4-methyl-1-pentene. The flask was evacuated for a short time to the vapor pressure of the solvents, and a premixed H_2–T_2 gas mixture was added to bring the system to 1 atm. pressure. The gas phase occupied the space directly over the reaction slurry. The rate of reaction of hydrogen was obtained by measuring the rate of addition of pure heptane required to maintain 1 atm. pressure in the flask (as indicated by a small inclined monometer). The gas samples were periodically withdrawn, swept directly into a CuO furnace, and collected in a water bubbler. These water samples were radioassayed to determine the change (if any) in the specific activity of the tritium. The data are shown in Table IV. It can be seen that the isotope effect in this reaction system is negligible.

TABLE IV
Determination of Isotope Effect

Sample	Time, min.	Volume H_2 reacted, ml.	Relative specific activity of gas sample, counts/sec.
1	20	13	199
2	41	25	200
3	64	38	188
4	85½	49	191
5	106	59	191
6	128	67	189
7	152	75	195
8	175	84	191

SUMMARY

Ziegler-Natta polymerizations conducted in the presence of tritium-labeled hydrogen gas produce polymers with approximately two labeled atoms per molecule. This observation supports the mechanism of Natta and co-workers which calls for addition of one hydrogen atom at each end of the polymer molecule.

Apparently, the catalyst hydride site formed during the termination reaction initiates high molecular weight polymer chains more readily than any catalyst alkyl linkages still remaining in the catalyst.

The tritium tracer technique was used to estimate a relationship between intrinsic viscosity and number-average molecular weight for poly-4-methyl-1-pentene. The relationship is:

$$[\eta] = 0.6 \times 10^{-4}(\bar{M}_n)^{0.92}$$

This is the only method we know of for determining this relation, and the technique may also be convenient for other Ziegler-Natta polyolefins that are too intractable to analyze by conventional means.

The authors would like to acknowledge valuable discussions held with Dr. R. Bacskai. Thanks are also due to Mr. W. F. Haddon who fractionated the polypropylene.

ADDENDUM

Since our preprint was submitted, we have continued to use the tritium-tracer technique to study the role of hydrogen in the propylene and 4-methyl-1-pentene polymerizations under similar experimental conditions. We investigated the possibility that the lower molecular weight polypropylene fractions might, in fact, only be labeled at one end of the chain. We also looked further into the scatter encountered in the heptane-soluble fractions of the poly-4-methyl-1-pentene $[\eta]$ - $\bar{M}_n$ relationship.

A series of five 4-methyl-1-pentene polymerizations was run at room temperature under partial pressures of tritium-labeled hydrogen of 0.3–1 atmosphere. The crude polymers were each separated in stepwise fashion into a boiling ether soluble (ES) polymer, boiling heptane soluble (HS), and heptane insoluble (HI) polymer. This separation technique differed from that used previously for this polymer where no ether extractions had preceded the heptane extractions. Also, in two previous runs the polymer soluble in isopropanol-HCl quench solution (QS) had been recovered; in the latest series an excess of methanol-HCl quench solution was employed, and no attempts were made to recover polymer from this solution.

We have obtained evidence from NMR, IR, x-ray, and melting point measurements which supports the conclusion that the ES fraction is essentially amorphous, i.e., atactic poly-4-methyl-1-pentene. The QS polymer visually resembled this fraction and is probably low molecular weight atactic material. The same type of measurements shows both the HS and HI fractions to be mainly crystalline, i.e., isotactic polymer.

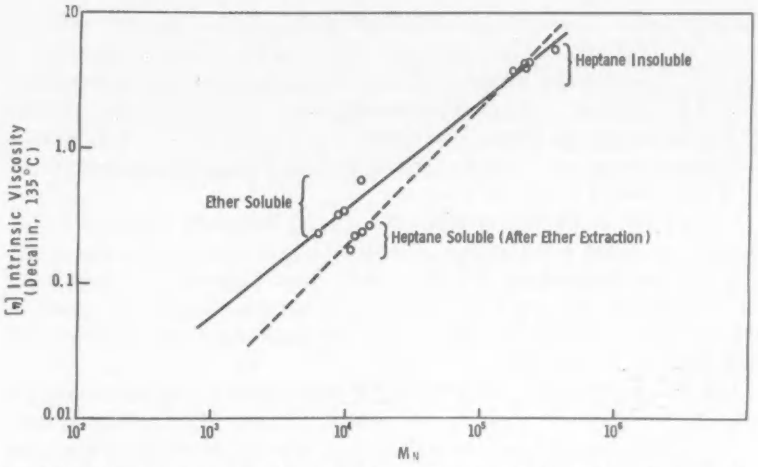

Fig. 3. Poly(4-methyl 1-pentene): $[\eta]$ vs. $\bar{M}_n$. Basis: two labeled chain ends/molecule.

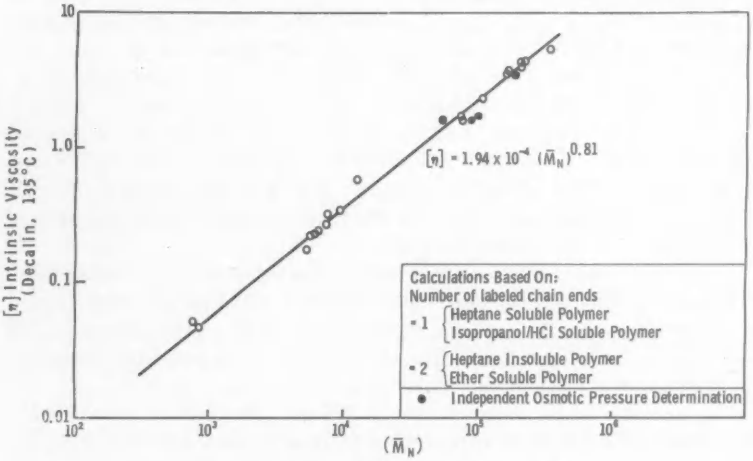

Fig. 4. Poly(4-methyl-1-pentene): $[\eta]$ vs. $\bar{M}_n$.

We were interested to find that in every case the HS polymer is lower in intrinsic viscosity than the corresponding ES polymer. There is similar evidence in the literature[11] of a drop in intrinsic viscosity with decrease in solubility for some polypropylene fractions.

The specific radioactivities (counts/min./mg.) of the ES fractions are in each case higher than the corresponding HS fractions. If the molecular weights are calculated on the basis of two labeled chain ends per molecule as before, the HS fractions appear to be higher in molecular weight than the ES fractions—a conclusion which is at variance with the intrinsic

viscosity data. These results are shown graphically in Figure 3. It is interesting to note that in the region of the ES and HS data for any intrinsic viscosity the molecular weights differ by about a factor of two between the ES and HS polymer. The data for the HS polymer can be brought into line by assuming only one labeled chain used for these fractions. This result is a little surprising, but it checks the trend of the data given in the preprint for a fractionated polypropylene.

In order to verify this assumption, we ran duplicate propylene polymerizations under 1 atmosphere of tritium-labeled hydrogen. The crude polymer was separated into ES, HS, and HI fractions in the same manner as for the poly-4-methyl-1-pentene. Once again the data showed that there is only one labeled end per molecule for the HS fraction and two labeled chain ends for the ES polymer.

The data presented in the preprint for poly-4-methyl-1-pentene may be included with the newest data, excluding the former heptane-soluble fractions. These fractions have been discarded, since IR data show them to be mixed isotactic and atactic polymers. Figure 4 shows the best fit of the data which yields the most reasonable $[\eta]$-$\bar{M}_n$ relationship. This relation is $[\eta] = 1.94 \times 10^{-4}(M_n)^{0.81}$. It is based upon polymer fractions which may have had a fairly broad molecular weight spread and therefore may not be as accurate as one based on narrow molecular weight fractions. However, it has been verified by independent high temperature osmotic pressure measurements*. Both of the QS and HS polymer molecular weights are calculated assuming one tagged chain end per molecule, while the ES and HI are based on two labeled chain ends. We have also assumed that the $[\eta]$-$\bar{M}_n$ relationship should be independent of the tacticity of the chains, as has been shown for polypropylene.[4]

The data indicate that the higher molecular weight fractions (HI and ES) of the respective isotactic and atactic portions of the polymer are labeled at both ends. The HI fractions represent over 95% of the polymer in all cases. This certainly suggests that the mechanism proposed by Natta and coworkers is the predominant one.

The lower molecular weight fractions (HS and QS) of the respective atactic and isotactic polymers appear to be formed by some secondary mechanism involving hydrogen in *either* the initiation *or* termination step but not in both. We can only speculate on what this mechanism might be. One possible explanation could be that the chains are initiated at a labeled site but grow to only a short length as the site becomes occluded or buried under the polymer; or, possibly, these chains are still growing when the reaction is quenched. It is also possible that the chains are initiated at a fresh, unlabeled catalyst-alkyl site and terminated rapidly with hydrogen due to the high activity of such a site. Other explanations may also be advanced. The correct mechanism must yield atactic (ES) and isotactic (HS) chains in the same range of molecular weights with the former labeled at both ends and the latter at only one end.

* Courtesy of Dr. A. Hiltz, Avisun Corp.

Conclusions

1. Ziegler-Natta polymerizations conducted in the presence of tritium-labeled hydrogen give polymers whose higher molecular weight fractions of both isotactic and atactic portions of the polymers contain approximately two labeled atoms per molecule. This observation supports the mechanism of Natta and coworkers as the predominant one in this type of polymerization.

2. There appears to be a secondary mechanism which produces the lower molecular weight fractions of both the isotactic and atactic portions of the polymers. This mechanism yields molecules with only one labeled end. Speculations are presented on the possible nature of this mechanism.

3. The tritium tracer technique was used to estimate a relationship between intrinsic viscosity and number-average molecular weight for poly-4-methyl-1-pentene. This relationship is $[\eta] = 1.94 \times 10^{-4}(\bar{M}_n)^{0.81}$. This is the first time to our knowledge that such a relationship has been presented in the literature. Furthermore, this is the only method we know of for determining this relationship and the technique may be applicable to other Ziegler-Natta polyolefins that are too intractable to analyze by conventional means.

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Synopsis

We have investigated the role of hydrogen as a chain length regulator in Ziegler-Natta polymerizations by use of tritium-labeled hydrogen. Natta and co-workers postulate a mechanism in which hydrogenation of a catalyst–growing chain bond occurs, yielding a catalyst hydride site and a dead chain with a hydrogen atom incorporated at the end. Subsequent initiation of a new polymer chain by the catalyst hydride site is also assumed in the mechanism. In the presence of tritium-labeled hydrogen, the polymer chains initiated by the catalyst hydride site and terminated by hydrogen should contain two tagged chain ends. Any other mechanism of initiation and/or termination could lead to only one or even no tagged chain end per molecule. Propylene was polymerized in the presence of tritium-labeled hydrogen and the polymer was fractionated; the tritium

content and intrinsic viscosities of the fractions were determined. The specific radioactivity (disintegrations/sec./g.) of the different fractions decreases as their intrinsic viscosities increase. We have established that tritium is not incorporated in significant amounts by exchange reactions and therefore is probably incorporated at the chain ends during initiation and termination reactions. The isotope effect for the reaction of hydrogen in these systems is being determined. The molecular weight of the polypropylene fraction may be calculated on the basis of values up to two for the number of tritium-labeled chain ends, and the best fit of the data to existing $[\eta]$-$\bar{M}_n$ relations yields the average number of chain ends initiated and terminated by hydrogen. Thus, by this technique we have been able to interpret in detail the mechanism suggested by Natta and co-workers. Furthermore, we have utilized the results obtained with polypropylene in obtaining the molecular weights of poly-4-methyl-1-1-pentene samples prepared in the presence of tritium-labeled hydrogen. We have correlated these with intrinsic viscosities. The tritium-labeling technique, therefore, also provides a convenient method for estimating the molecular weight of Ziegler-Natta polyolefins that are too intractable to analyze by other means.

Résumé

Nous avons étudié le rôle de l'hydrogène comme régulateur de chaîne au cours de polymérisations de Ziegler-Natta, à l'aide de l'hydrogène marqué au tritium. Natta et collaborateurs postulent un mécanisme dans lequel a lieu l'hydrogénation de la liaison entre le catalyseur et la chaîne en croissance, produisant un site hydrure du catalyseur et une chaîne morte avec un atome d'hydrogène incorporé à l'extrémité. On suppose aussi dans le mécanisme qu'une initiation subséquente d'une nouvelle chaîne polymérique se fait par ce site-catalyseur. En présence d'hydrogène marqué au tritium, les chaînes polymériques initiées par le site hydrure-catalyseur et terminées par l'hydrogène devraient contenir deux extrémités marquées. Tout autre mécanisme d'initiation et de (ou de) terminaison ne conduisent qu'a une ou aucune extrémité marquée par molécule. On a polymérisé du propylène en présence d'hydrogène contenant du tritium et le polymère a été fractionné; on a déterminé la teneur en tritium et les viscosités intrinsèques des fractions. La radioactivité spécifique des différentes fractions (désintégrations/sec/g) diminue quand leur viscosité augmente. Nous avons établi que le tritium n'est pas incorporé en quantités significatives par réactions d'échange et de ce fait est probablement incorporé aux extrémités de chaînes au cours des réactions d'initiation et de terminaison. L'effet isotopique pour la réaction de l'hydrogène dans ces systèmes est déterminant. Le poids moléculaire d'une fraction de polypropylène peut être calculé sur la base des valeurs limitées à deux pour les nombres d'extrémités caténaires marquées au tritium, et la meilleure adaptation des résultats aux relations existantes $[\eta]$ - $\bar{M}_n$ donne le nombre moyen d'extrémités de chaînes initiées et terminées par l'hydrogène. Par cette technique nous avons donc été amené d'interprêter en détail le mécanisme suggéré par Natta et ses collaborateurs. En plus, nous avons utilisé les résultats acquis avec le polypropylène en obtenant les poids moléculaires d'échantillons de poly-4-methyl-1-1-pentene, préparés en présence d'hydrogène tritié. Nous avons mis ceux-ci en corrélation avec les viscosités intrinsèques. La technique de marquage au titrium fournit de ce fait aussi une méthode convenant pour l'estimation des poids moléculaires de polyoléfines Ziegler-Natta, qui sont trop intraitables pour être analysées par d'autres moyens.

Zusammenfassung

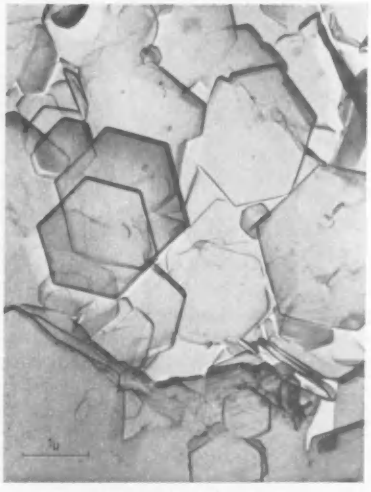
Die Rolle des Wasserstoffes als Kettenlängenregulator bei der Ziegler-Natta-Polymerisation wurde unter Verwendung von tritium-markierten Wasserstoff untersucht. Natta und Mitarbeiter stellten einen Mechanismus mit Hydrierung der Bindung zwischen Katalysator und wachsender Kette unter Bildung einer Katalysator-Hydridbindung und einer toten Kette mit eingebautem Wasserstoffatom am Ende auf. Auch

ein Start einer neuen Polymerkette durch das Katalysator-Hydrid wird bei diesem Mechanismus angenommen. In Gegenwart von tritium-markierten Wasserstoff sollten die an einer Katalysator-Hydridstelle und durch Wasserstoff abgebrochenen Polymerketten zwei markierte Kettenenden enthalten. Jeder andere Start- oder Abbruchsmechanismus kann nur zu einem oder keinem markierten Kettenende pro Molekül führen. Propylen wirde in Gegenwart von tritium-markiertem Wasserstoff polymerisiert und das Polymere fraktioniert; der Tritiumgehalt und die Viskositätszahl der Fraktionen wurde bestimmt. Die spezifische Aktivität (Zerfälle/sek/g) der verschiedenen Fraktionen nimmt mit steigender Viskositätszahl ab. Es wurde festgestellt, dass kein merklicher Tritium-Einbau durch Austauschreaktionen stattfindet und der Einbau daher wahrscheinlich an den Kettenenden bei der Start- und Abbruchsreaktion erfolgt. Der Isotopeneffekt bei der Reaktion des Wasserstoffs in diesen Systemen wird bestimmt. Das Molekulargewicht der Polypropylenfraktionen kann auf Grundlage der Zahl der tritiummarkierten Kettenenden, und zwar mit Werten bis zu zwei, berechnet werden und die bestmögliche Angleichung der Daten an bekannte $[\eta]$-$\bar{M}_n$-Beziehungen liefert die mittlere Zahl der durch Wasserstoff gestarteten und abgebrochenen Kettenenden. Mit diesem Verfahren war es möglich den von Natta und Mitarbeitern vorgeschlagenen Mechanismus in seinen Einzelheiten zu überprüfen. Ausserdem wurden die an Polypropylen erhaltenen Ergebnisse zur Ermittlung des Molekulargewichts von Poly-4-methylpenten-1-1-proben benützt, die in Gegenwart von tritium-markierten Wasserstoff dargestellt worden waren. Eine Korrelation mit Viskositätszahlen wurde hergestellt. Das Tritium-Markierungsverfahren liefert so auch eine brauchbare Methode zur Bestimmung des Molekulargewichts von Ziegler-Natta-Polyolefinen, die auf andere Weise nicht untersucht werden können.

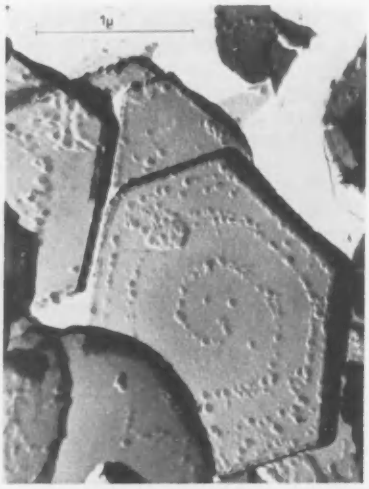
Discussion

A. Schindler (*Camille Dreyfus Lab., Durham, N. Car.*): How was it proved that no tritium hydrogen exchange occurs in the polymer chain?

A. S. Hoffman: We have shown that the tritium exchange reaction is negligible with preformed polymer chains. Such chains are presumably not associated with active catalyst sites.



Discussion Fig. 1.



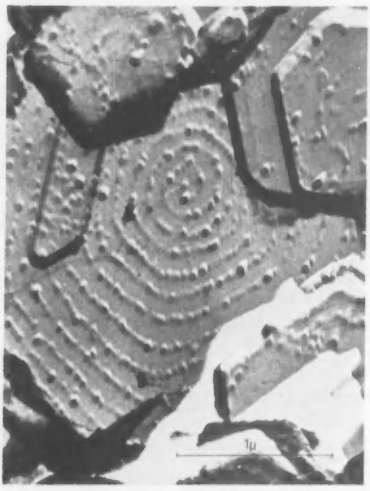
Discussion Fig. 2.

Discussion Fig. 3.

A. Schindler: With the addition of dead polymer chains to an active catalyst system, an exchange reaction cannot be expected to take place, since it is the hydrogen on the β-carbon of the bridging alkyl group in the bimetallic catalyst complex which shows the ability for exchange reactions in the case of deuterium.

A. S. Hoffman: It is true that we have not been able to estimate the magnitude of exchange reactions with the beta hydrogen of a growing polymer chain. This is a point which would be interesting to study further.

In any case, by means of independent osmotic pressure measurements we have been able to verify our $[\eta]$-$\bar{M}_n$ relationship for poly-4-methyl-1-pentene in the range of



Discussion Fig. 4.

[η] from 1.6 to 3.6. In this range we have assumed two tritium-labeled hydrogens per chain in calculating $\bar{M}_n$. In order that the exchange reaction predominate, as your deuterium data indicate, only one of the initiation or termination steps can incorporate tritium into the polymer, not both. It does not appear reasonable to us at this time to neglect either one of these steps as a source of tritium.

L. S. Rayner (*I.C.I. Ltd., Herts, Great Britain*): Have either Mr. Hoffman or Monsieur Bourat observed a change in propylene polymerization rate in the presence of hydrogen? I ask this question because while it is known in the literature that hydrogen *lowers* the polymerization rate of propylene in contact with $-TiCl_3$, we have observed *higher* rates with other types of $TiCl_3$. Do you have any comment on this?

A. S. Hoffman: We have not investigated the effect of hydrogen on the rate of polymerization of propylene.

L. A. M. Rodriguez and J. A. Gabant (*Union Carbide European Research Associates, Brussels, Belgium*): In a previous publication (B. Hargitay, L. Rodriguez, and M. Miotto, *J. Polymer Sci.*, **35**, 559 (1959)), experiments aiming to localize the active centers of an α-$TiCl_3$-$Al[CH_3]_3$ catalyst, were described. In these experiments, optical microscopy was used to examine the polymerization of ethylene on large sublimed α-$TiCl_3$ crystals.

In a more recent work, electron microscopy allowed us to follow the polymerization on small α-$TiCl_3$ crystals, as formed by direct reduction of $TiCl_4$ with hydrogen. Figure 1 shows a carbon replica of such crystals. These crystals appear as more or less regular hexagonal leaflets of which the large (00.1) faces show practically no structural details.

After the reaction between α-$TiCl_3$ and $Al(CH_3)_3$ alone no change is observed. Hence the catalyst formed is indistinguishable by electron microscopy from pure α-$TiCl_3$ crystals, although it is known (unpublished work) that under the conditions used the whole surface of the crystals has in fact reacted. It seems probable, therefore, that the modifications due to the reaction are too small to be observed by electron microscopy.

Replicas obtained after polymerization (of propylene, for instance) on the catalyst show the presence of many dots which are the traces of the polymer. Figures 2, 3, and 4 demonstrate clearly that these dots are localized along a spiral which is almost certainly a growth spiral. Such growth spirals may be observed after a limited attack on $TiCl_3$ crystals prior to reaction with $AlMe_3$ and polymerization.

It may be inferred from this that the active centers of polymerization are not situated on the (00.1) face itself, which has completely reacted with $AlMe_3$, but along the growth spirals. In fact, it is very unlikely with the system used that the active centres exist outside the spiral and that the polymer formed migrates to the spiral step.

These results support the previously proposed idea that the active centers are located on faces where titanium atoms are directly accessible to the aluminum alkyl and to the monomer.

A. Nicco (*France*): Est-ce qu'il y a du polymère formé sur les faces latérales des cristaux hexagonaux?

L. A. M. Rodriguez: Il n'est malheureusement pas encore possible de répondre à votre question. La difficulté provient de ce que les spirales de croissance situées sur le plan basal 00.1 viennent, le plus souvent, mourir tangentiëllement aux faces latérales, en sorte qu'il n'est pas aisé d'attribuer les sites de polymérisation qui existent au pourtour des cristaux, aux faces qui constitutent la spirale ou aux faces latérales proprement dites.

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Physical Restrictions on the Rate of Polymerizations by Some Stereospecific Catalysts

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The initiation of polymerization by a catalytic surface leads to complications in the kinetics not present in truly homogeneous polymerizations. This is particularly so if the macromolecules are chemically bound to sites on the catalyst surface during growth, as occurs in the case of Ziegler-Natta mixed catalysts for the stereospecific polymerization of alkenes and vinyl derivatives.[1,2]

It is possible to distinguish a number of steps in the kinetic scheme: (*1*) transport of monomer to the catalyst surface, (*2*) possible pre-adsorption of the monomer on the catalyst surface, (*3*) the growth or propagation reaction, in the case of the Ziegler-Natta catalysts this is:

$$\mathrm{Cat(C_2H_3X)_nR + CH_2{=}CHX \rightarrow Cat(C_2H_3X)_{n+1}R}$$

(*4*) the breaking of the bond between the macromolecule and the catalyst, thereby terminating growth, either (*a*) spontaneously:[3]

$$\mathrm{Cat(C_2H_3X)_nR \rightarrow Cat{-}H + CH_2{=}CX(C_2H_3X)_{n-1}R}$$

or (*b*) by transfer, with monomer, for instance:[3]

$$\mathrm{Cat(C_2H_3X)_nR + CH_2{=}CHX \rightarrow Cat\ C_2H_4X + CH_2{=}CX(C_2H_3X)_{n-1}R}$$

(*5*) possible desorption of the broken-off macromolecules, and (*6*) transport of macromolecules away from the catalyst surface.

Any of these processes can in principle become the rate-controlling step with the exception of (*4*), which, as it normally regenerates a catalytically active bond, does not significantly affect the overall rate of polymerization —merely the average molecular weight of the product.

Catalyst-clearing processes, (*5*) and (*6*), can control the rate of polymerization since if they are slow the consequences react on earlier processes: (*6*) on (*1*) and (*5*) on (*2*). It is difficult to be sure about the importance of the adsorption–desorption processes. However, if adsorption of the monomer in the neighborhood of the reaction site is important—and it has often been suggested that this has a vital influence on the stereospecificity of many catalysts[4]—then the macromolecules, breaking away from the growth sites, have an unsaturated group adjacent to the surface and are likely to compete for the adsorption sites. It is possible, for instance, that in the monomer transfer reaction, the macromolecule may fill the adsorption site

vacated by the displacing monomer molecule, block this site for further adsorption of monomer, and hence prevent or hinder the feeding of monomer to the adjacent growth site. The situation is clearer with the transport processes. There are a number of cases where the interplay of processes (*6*) and (*1*) is doubly manifest in the visible encapsulation of the catalyst particles by polymer gel and the concurrent deceleration of the rate of polymerization. Such a situation occurs in a system studied in our laboratories: deetherated Grignard reagent particles, surface-modified by reaction with titanium tetrachloride and heat-conditioning at 150°C.,[5,6] polymerize styrene at a decelerating rate with the catalyst particles, originally some 30–100 μ in diameter, becoming encased in capsules of gel up to 50 μ thick. Similar decelerating rates which have been attributed to polymer accumulation or the onset of diffusion control have been reported for the polymerization of propylene by a catalyst derived from vanadium oxychloride and triisobutylaluminum,[7] of ethylene by aluminum gauze and titanium tetrachloride,[8] and styrene and 4-methyl-1-pentene by triisobutylaluminum and titanium trichloride.[9] The deceleration was also observed in the polymerization of ethylene at constant pressure by a triethylaluminum–titanium tetrachloride catalyst,[10] and for styrene by triethylaluminum–titanium tetrachloride[11]—though here attributed to a parallel catalyst deactivation reaction. The most interesting results relevant to the present discussion are those of Burnett and Tait[12] for styrene. If the catalyst is made from diethylaluminum chloride and α-titanium trichloride the conversion curve is very similar to ours (Fig. 1), the rate rapidly decreasing to a steady value at around 200 min., though, the catalyst being more active, this corresponds to a higher conversion than in our experiments. Photomicrographs revealed the deposition of polymer on the catalyst and consequent agglomeration of the particles. If triethylaluminum was used to make the catalyst then there was an acceleration during the first few hours, attributed to continuing reaction of the catalyst components, the reaction mixture being used and not the washed solid product. In undiluted monomer a steady rate ensued. If, however, the monomer was diluted to 4*M* with *n*-heptane, the typical deceleration was observed.

MODEL KINETIC SYSTEMS

1. Progressive Invasion of the Catalytic Surface by a Gel of Constant Monomer Concentration

This is the simplest model possible and very similar to the classic treatment of surface reactions with catalyst poisoning. It is assumed that the concentration of monomer in the liquid phase remains constant, a reasonable approximation as we are only considering low conversions (up to 5%). It is also assumed that the concentration of monomer in the gel phase at the catalyst surface remains constant. The most obvious physical realization of this concept would be if the diffusion of monomer within the gel and across the liquid–gel interphase were rapid compared with rates of reaction

and adsorption so that a quasi-equilibrium partition of monomer between the two phases is established. This can only be an approximation to the true situation. Obviously true equilibrium is not established, since the polymer and monomer of styrene are miscible in all proportions; the requirement is merely that the concentration of monomer in gel c_g remains constant throughout the gel within experimental error as long as the concentration in the liquid phase c_l remains constant. The rate of polymerization of monomer is therefore:

$$R_p = k_p (1 - \alpha) nc_l + k_p \alpha n c_g \tag{1}$$

where n is the number of moles of active sites per catalyst sample and α the fraction of them encased by gel. k_p is the propagation constant in (moles/catalyst sample)$^{-1}$ min.$^{-1}$ and is assumed to be the same in both phases. The initial rate and steady-state rate, corresponding to complete coverage of the catalyst, respectively, are given by:

$$\begin{aligned} R_{p_0} &= k_p n c_l \\ R_{p_s} &= k_p n c_g \end{aligned} \tag{2}$$

If x is the percentage conversion, the rate of polymerization is:

$$dx/dt = (1 - \alpha) R_0 + \alpha R_s \tag{3}$$

R_0 and R_s being the initial and steady-state rates, respectively, in per cent polymerization/min. α is obviously a function of x:

$$\begin{aligned} \alpha &= 0, x = 1 \\ \alpha &= 1, x \geq x_s \end{aligned} \tag{4}$$

x_s being the conversion at which complete coverage and the steady rate are attained. The simplest assumption is that:

$$\alpha = x/x_s, x \leqslant x_s \tag{5}$$

Another possibility in view of the fact that we are dealing with the deposition of the product on the surface is:

$$\alpha = (x/x_s)^{2/3} \tag{6}$$

We take the simpler alternative (5). The rearranged differential conversion equation is thus:

$$dx/dt = R_0 + (R_s - R_0)(x/x_s) \tag{7}$$

Integrating between 0 and x gives:

$$t = \frac{x_s}{R_s - R_0} \ln \left[1 - \left(1 - \frac{R_s}{R_0} \right) \frac{x}{x_s} \right], x \leqslant x_s \tag{8}$$

A fit of this equation to a dilatometric run, with 0.1 *g.* C_3H_7MgBr–$TiCl_4$ heat-treated catalyst and undiluted styrene at 35°C., is shown in Figure 1. The equation is not universally compliant: fixing any two of the experi-

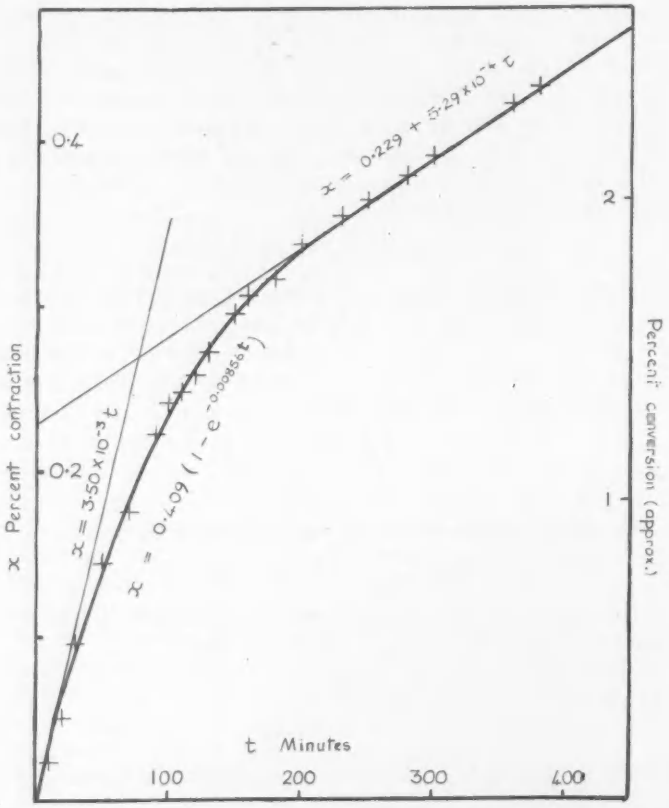

Fig. 1. Conversion curve for an experiment with undiluted styrene catalyzed by an ether-free propylmagnesium bromide–titanium tetrachloride, heat-cured, catalyst. The asymptotic rate and the convergence point are estimated from the experimental points. The initial rate and the conversion curve are calculated from this data on the assumption that the monomer concentration in the gel phase is constant and that the gel encroaches over the catalyst particles until they are completely encapsulated at the convergence point. The points shown are experimental.

mental parameters, R_s, R_0, and x_s, determines the third. Since the early stages of the polymerization were affected by settling and mixing inconsistencies, we have estimated the steady rate, R_s, and the convergence point, x_s, from the experimental data (points on Fig. 1) and calculated R_0 and the theoretical curve.

Although the fit of the curve and the value of R_0 are excellent, there are doubts. First of all, exponential equations of this type are very accommodating. This is probably the reason why assumption (5) fits while assumption (6) is probably more correct. There are more serious doubts

about the physical significance of the fit. An equation of the type (2) might arise from an adsorption–desorption mechanism. It is also uncertain whether the model is realistic. Unlike the usual case of a catalytic reaction with catalyst poisoning the two processes are not competitive, but inherently concomitant; the catalyst is in fact blocked by the growth reaction. It might be argued, then, that the gel grows not as spreading islands of substantial depth but as a coherent film, established early in the reaction, and progressively thickening. The deceleration is then due to diffusion-control and the increasing path for diffusion of monomer from the liquid phase through the gel to catalyst surface.

2. Coherent, Thickening Film Model with Diffusion Control. General Considerations

One diffusion-controlled mechanism has been postulated. Pasquon, Dente, and Narduzzi[7] have fitted their data for propene polymerization on a $VOCl_3$–$Al(i\text{-}C_4H_9)_3$ catalyst to an equation of the type:

$$1/R_p = A + Bx \tag{9}$$

The geometry of their model is vague: the diffusion equations used appear to be those for planar diffusion, which, if so, are inappropriate for a spherical model.

The integrated form is:

$$t/x = A + B'x \tag{10}$$

(A, B, and B' are constants). The plot of t/x against x is not linear at any stage, not even during the steady state, in our system, whether the monomer is diluted with hexane or not.

The rate of diffusion of the monomer through the encapsulating gel is available in principle from the solution of Fick's Second Law of Diffusion:

$$D\nabla^2 c = \partial c/\partial t \tag{11}$$

in appropriate coordinates and with appropriate boundary conditions for the concentration of monomer, c, at the surface of the catalyst particle and the surface of the capsule. In eq. (11) it is assumed that the diffusivity D is independent of the composition of the gel. This simplification is justifiable at the present level of discussion, in that we are still seeking to establish the origin and general character of the phenomenon. Further simplifications are necessary. We have to regard the catalyst particles and gel capsules as uniform concentric spheres of radii a and ρ respectively, changes in volume on polymerization and solution of polymer in monomer are ignored and a steady state in diffusion fluxes is assumed, i.e.,

$$\partial c/\partial t = 0 \tag{12}$$

This assumption, whose validity is difficult to assess, supposes that relaxation times for the re-establishment of a stationary state in fluxes following changes in radius, ρ, or boundary concentration, c_ρ are small compared

with the time for change of these parameters. Assumption (12), implying that the mass of monomer passing each concentric shell of radius r per unit time is constant, reduces the diffusion equation to:

$$-dc/dr = B/r^2 \tag{13}$$

thus:

$$c = A + B/r \tag{14}$$

Substituting the boundary concentrations c_a, c_ρ yields:

$$c_a = c_\rho + B\,[(1/a - 1/\rho)] \tag{15}$$

Assuming that the rate of polymerization per particle to be diffusion-controlled and equal to the rate of delivery of monomer to the surface:

$$R_p' = -D(dc/dr)_{r=a} = DB/a^2 \tag{16}$$

The rate of reaction per particles then

$$R_p' = k_p c_a\, 4\pi\, a^2 n' = k_p' c_a a^2 \tag{17}$$

where k_p is again the surface propagation constant and n' is the number of moles of active centers per unit area of catalyst surface. Equating the right-hand sides of eqs. (16) and (17) and substituting for B in eq. (15) yields:

$$c_a = \rho D c_\rho / [(D + k_p' a^3)\,\rho - k_p' a^4] \tag{18}$$

which together with eq. (17) gives the rate of polymerization in terms of constant parameters a, D, k_p', the time-dependent capsule radius ρ and the boundary concentration c_ρ.

3. Coherent, Thickening Film Model: Boundary Conditions for the Diffusion Equations

It is exceedingly difficult to define the conditions prevailing at the boundary of the capsule as it advances out into the supernatant liquid from the catalyst surface. The boundary is visibly well defined and most persistent when the gel is digested with boiling solvent at the end of the run. The only obvious simplification is that concentration of monomer in the supernatant phase may be taken as constant over the low conversions used, and that since the volume of this phase is greatly in excess of that of gel the concentration of polymer in the supernatant liquid remains low. Two possibilities are that the concentration of polymer at the surface of the capsule has a critical value or that it is in excess of a certain critical value. Though it is little more than an *ad hoc* assumption we use the former in future discussion and set the concentration of monomer at the boundary as constant.

4. Growth Equations for the Diffusion-Controlled Model

If c_ρ is assumed to be constant over the period under consideration, it will be seen that eq. (18) will tend to a constant value, independent of the

capsule radius ρ: $Dc_\rho/(D + k_p'a^3)$, as ρ increases and this will correspond to a steady state in rate of polymerization. We are unfortunately not in a position to measure the rate of growth of the capsules and so have to find how ρ varies with time.

A general linear growth function obeyed by some systems: (e.g., metal oxidation, crystal growth) is:

$$\rho = a + \beta t \tag{19}$$

which, if substituted in eqs. (18) and (17) leads to a form:

$$dx/dt = Q(a + \beta t)/(a + P\beta t)$$

or

$$x = Q\{t + a\,(1 - 1/P)[\ln\,(1 + P\beta t/a)]/\beta\}/P \tag{20}$$

where P, Q, and β are constants. Although this equation tends to a constant asymptotic rate we have established[6] that it is not capable of fitting a rapid convergence of the type found experimentally.

An alternative growth equation assumes that the rate of increase in volume of the capsule is proportional to the rate of polymerization per particle:

$$dV/dt = AR_p'$$

$$\rho^2 d\rho/dt = Bk_p'c_a a^2 \tag{21}$$

Substituting in eq. (18) and integrating gives:

$$A'(\rho^3 - a^3) - B'(\rho^2 - a^2) = k_p'c_\rho t \tag{22}$$

The roots of eq. (22) are too complicated for curve fitting, so the assumption that the volume of the capsule is proportional to the conversion is used again:

$$\rho^3 - a^3 = A''x$$

and

$$A'A''x - B'(A''x - a^3)^{2/3} + B'a^2 = k_p'c_\rho t \tag{23}$$

which is still too complicated for practical purposes. The approximation to

$$A'A''x - B'(A''x)^{2/3} = k_p'c_\rho t \tag{24}$$

has been tested by plotting $t/x^{2/3}$ against $x^{1/3}$ but is only linear during the steady-state region (Fig. 2).

A less drastic approximation leads to:

$$A'A''x - B'(A''x)^{2/3}\,(1 - 2a^3/3A''x) = k_p'c_\rho t$$

or

$$t/x^{2/3} = Fx^{1/3} - G + H/x \tag{25}$$

which, as x becomes large, tends to the asymptote:

$$(t/x^{2/3})_{\text{asym}} = Fx^{1/3} - G \tag{26}$$

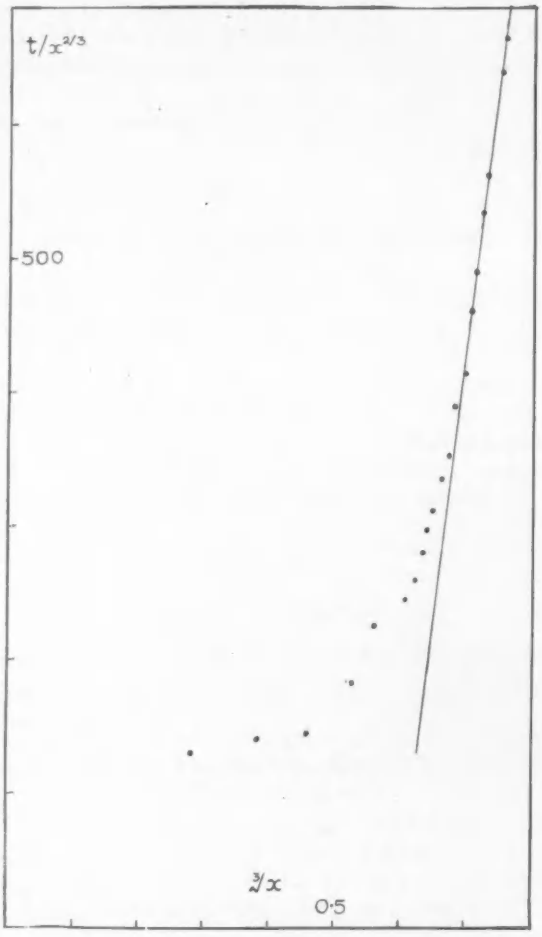

Fig. 2. Plot of $t/x^{2/3}$ against $x^{1/3}$ for the experimental data shown in Fig. 1.

enabling H to be evaluated from the deviation of the curve from the extrapolated asymptote:

$$t/x^{2/3} - (t/x^{2/3})_{\text{asym.}} = H/x \tag{27}$$

The slope and intercept of the asymptote in Figure 2 give F as 4380 and G as 2650. Plotting the deviation from the asymptote against $1/x$ according to eq. (27) gives a good straight line except for the three points corresponding to reaction times under 30 min., but it does not pass through the origin and instead of an equation of the form (27) it is:

$$t/x^{2/3} - (t/x^{2/3})_{\text{asym.}} = 150/x - 435 \tag{28}$$

and so eqs. (25) and (26) become:

$$t = 4380x + 150x^{-1/3} - 3085x^{2/3} \quad x \leqslant 0.345$$

and

$$t = 4380x - 2650x^{2/3} \qquad x \geqslant 0.345 \qquad (29)$$

The inequality of the coefficients of $x^{2/3}$ arises from the intercept in the plot of eq. (27), and because of it the curve does not converge on the asymptote at $x = 0.345$ but crosses it (Fig. 3).

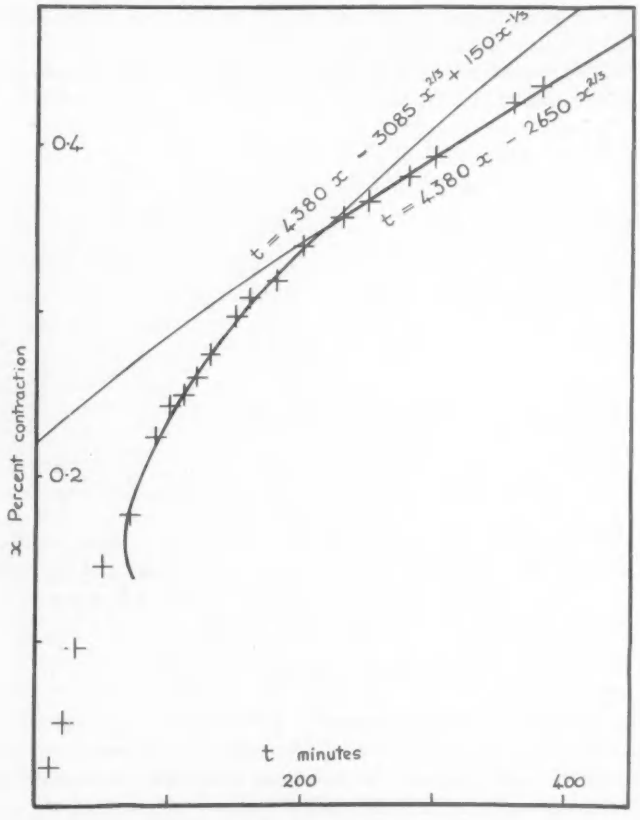

Fig. 3. Conversion curves for the experimental data shown in Fig. 1 calculated for a diffusion-controlled model assuming that the capsule-radii are determined by accumulation of all the polymer formed. The lines are calculated; the points are experimental.

The deviation below 70 min., though most pronounced, is trivial and arises from the breakdown of the assumption that $a \ll \rho$. A better fit could be obtained by including more terms in the expansion of eq. (23) and

not neglecting the term $B'a^2$. The deviation above $x = 0.345$ is a more fundamental misfit and must arise from a limitation of the model.

Phenomologically the misfit arises from the same cause as the failure to fit the linear growth function, but since the model has a definite physical basis the negative results are more instructive. These equations cannot reproduce the convergence of the curve to a steady rate at a relatively low time of reaction. The implication is that the steady state is set up earlier than, and for reasons other than, the asymptotic convergence of eq. (18) as ρ increases monotonously with time according to eq. (19) or (22). Assuming constant catalyst activity, some other factor must be acting to limit the increase in ρ, and this is almost certainly elution of polymer from the capsules.

It is possible to modify eqs. (21) to allow for a rate of elution proportional to the surface area of the capsule:

$$dV/dt = AR_p' - B\rho^2$$

$$\rho^2(B' + d\rho/dt) = A'k_p'c_a a^2 \tag{30}$$

but the solution of eq. (30) is too complicated for practical purposes.

It is also possible to assume that the stationary state in rate corresponds to a stationary state in capsule size so that in eq. (30)

$$d\rho/dt = 0$$

and

$$c_a = A''\rho_s^2/k_p'a^2$$

and

$$R_s' = A''\rho_s^2 \tag{31}$$

R_s' is the steady-state rate of polymerization per particle, and is not directly proportional to the rate coefficient. It is not independent of it, since the value of ρ_s, the stationary-state radius, is a complicated function of k_p, D, and a. Little more can be said about this model.

DISCUSSION

One of the most interesting aspects of the problem of the encapsulated catalyst particle is the formation of the capsule. It cannot be a true solubility effect since polymer and monomer of styrene are miscible in all proportions, but rather a rate of solution effect. Admittedly, the rate of polymerization is not particularly rapid; the chemically controlled process requires an activation energy,[5] and the pre-exponential factor is likely to be low,[13] but the rate of dissolution of polymer must be slower still. There are two pieces of evidence to support this contention: the experimental fact that although the molecular weight of the polystyrene is not excessive ($1\text{–}2 \times 10^5$), the capsules are exceedingly difficult to dissolve in good solvents under nondegradative conditions, and the postulated mechanism

which involves the rooting of the growing molecules to the catalyst. Only a small proportion of the macromolecules in the capsule can be so rooted, but entanglement of the unbound molecules with the bound ones must be a retarding influence on their escape into the liquid phase. Macromolecules adsorbed on the catalyst could act in the same way. This does in fact seem to be the explanation, for if the catalyst–polymer bonds are broken by treatment with ethanolic HCl, then the resistance of the polymer to dissolution disappears.

There are other possible explanations for the deceleration: chemical deactivation of the catalyst[11] either by impurities or intrinsic side reaction, blocking of the catalyst site by adsorption, or the coagulation of the gel-encased particles.[12] The main reason for prefering an encapsulation theory is that the catalyst particles were much larger than those of other workers (ca. 50 μ, as compared to 6 μ in Burnett and Tait's system,[12] for example) and the growth of capsules was clearly visible. We are also sure that no appreciable coagulation occurred, though this did cause trouble in earlier work where stirring was insufficient.[5] Catalyst destruction by impurities is likely to be an instantaneous reaction with such reactive catalysts and we do not see a way in which styrene, propene, and ethylene can react other than by reactions (*3*), (*4a*), and (*4b*), which are catalyst-regenerating processes. A straight-forward adsorption mechanism would obey some form of the adsorption isotherm:

$$\alpha = x/(A + Bx)$$

$$dx/dt = A'\alpha + B'(1 - \alpha)$$

rather than the simpler eqs. (5) and (7).

More positive evidence for the encapsulation theory may be found in the results of Burnett and Tait.[12] One catalyst system which was not autoretarding in pure styrene was so if the styrene was diluted with heptane. In our system the steady rate was attained earlier and at a lower conversion if the styrene was diluted with heptane, hexane, or benzene, but undiluted styrene always showed deceleration. A nonstereospecific modification of the catalyst,[5] which gave polymer of much lower molecular weight (ca. 10^4) did not exhibit autoretardation or encapsulation. A nonstereospecific modification of the catalyst[5] giving a polymer of analogous molecular weight (ca. 10^5) did show autoretardation. This again indicates that dissolution rather than adsorption restrictions are the source of the deceleration. Adsorption may assist in the formation and stabilization of the capsules. The variation in encapsulation effects with different catalysts may be due to this, but may equally well be due to differences in the specific rates of polymerization and termination.

It is not possible to distinguish between the two encapsulation mechanisms discussed. Doubts about the partition model were listed in that section. The difficulties with the diffusion model are the unworkability of the functions derived for the more realistic of the model and the far more

fundamental problem of choosing a valid boundary condition for the monomer concentration at the surface of the capsule. We cannot, therefore, dismiss the diffusion-controlled mechanism on the grounds that we cannot fit the data. There is one piece of evidence, however, which does support the partition model rather than a diffusion-controlled mechanism. At higher temperatures the onset of the steady rate is much later than at lower temperatures. At 75°C. it is not attained at all. If, however, the steady-state rate is first attained at a lower temperature, the rate remains steady, at a higher value, if the run is continued at 75°C. The effect is obviously then not due to chemical deactivation at the higher temperature. If the deceleration was due to diffusion restrictions, then the steady rate must correspond to a stationary state in the rate of diffusion to the catalyst and perhaps even in the capsule radius. Since diffusion and dissolution processes accelerate with temperature, the steady rate should be attained earlier at the higher temperature. The encroachment of a gel phase over the catalyst surface could well be more rapid at a lower temperature (that is if the temperature coefficient for dissolution is greater than that for polymerization). Once the capsule is complete, the catalyst is likely to remain covered, even if the temperature is raised, and so the steady rate can be measured even at the higher temperatures. Provided the steady state was first attained, the energy of activation for a given catalyst–monomer–solvent system is reproducible and independent of the direction in which the temperature is varied.[6] This is easily understandable on a partition model, where the observed energy of activation is a function of that for propagation and the temperature coefficient of the concentration of monomer in the gel.

Despite serious doubts about the actual mechanism of retardation by encapsulation there are several unavoidable conclusions.

A rate coefficient in a heterogeneously catalyzed polymerization cannot be assumed to refer to a chemical reaction unless it is certain that encapsulation or adsorption effects do not have the controlling influence. A steady rate from the beginning of the reaction is not conclusive evidence for chemical control, since encapsulation may be set up very early before settling and mixing inconsistencies have died out, or the deceleration may be masked by acceleration effects of the type reported by Burnett[12] and Natta.[14] Similarly mechanistic arguments based on copolymerization reactivity ratios[15] depend on the assumption that the rate of reaction at the active bond is in fact determining the relative rate of monomer consumption and not differences in diffusion rates, dissolution in the gel phase, or adsorption. These effects are not necessarily avoided if the system is initially homogeneous. A deceleration is observed in the polymerization of methyl methacrylate initiated by solutions of Grignard reagents.[16] It has been attributed to the precipitation of polymer, which carries the active centers with it into a gel phase. The effect disappears if homogeneous conditions are maintained throughout the polymerization.

Encapsulation is unlikely to effect stereospecificity, but adsorption of polymer on the catalyst could well have a profound effect. Encapsulation

will cause a reduction in molecular weight if the spontaneous termination process (*4a*) is important, but it should not have any effect if termination is by monomer transfer (*4b*).

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Synopsis

A steady decline in rate is often observed in polymerizations catalyzed by solid Ziegler-Natta catalysts and related types. In some instances this may be the result of chemical deactivation of the catalytic sites, but in others, as has been recognized for a number of years, the cause is most obviously due to the encapsulation of the catalyst particles and the consequent restriction in diffusion of monomer on to the catalyst site. A detailed and precise general treatment is practically impossible, because of the lack of knowledge about the physical conditions prevailing at the surface and in the interior of the gel phase. Certain model systems are considered and their applicability to known cases discussed. In certain cases a pseudo-steady state in rate of polymerization by encapsulated catalyst particles is observed. The conditions under which this may arise are examined. Analogous effects arise in initially homogeneously catalyzed polymerizations such as methyl methacrylate initiated by Grignard reagents, if the polymer is allowed to precipitate, as the precipitating polymer carries the active sites out of solution.

Résumé

On observe souvent une diminution régulière de la vitesse dans les polymérisations catalysées par des catalyseurs solides du type Ziegler-Natta et par d'autres catalyseurs apparentés. Dans certains cas ce phénomène peut résulter d'une désactivation chimique des sites catalytiques, mais dans d'autres cas, comme cela est reconnu depuis un certain nombre d'années, le phénomène est plus spécialement causé par un englobement des particules de catalyseur ce qui entraîne une diminution de la diffusion du monomère vers le site catalytique. Une étude détaillée et précise est pratiquement impossible du fait du manque de connaissances en ce qui concerne les conditions physiques qui prévalent à la surface et à l'intérieur de la phase gélifiée. Certains systèmes de référence sont considérés et leur application à des cas connus est discutée. Dans certains cas on observe un pseudo-état d'équilibre dans la vitesse de polymérisation par des particules de catalyseur englobées. On a examiné les conditions dans lesquelles ce phénomène peut se produire. Des effets analogues se présentent lors de polymérisations

catalysées initialement de manière homogène telles que celle du méthacrylate de méthyle initiée par des réactifs de Grignard quand on laisse précipiter le polymère, ce dernier entraînant dans sa précipitation les sites actifs de la solution.

Zusammenfassung

Bei der Katalyse von Polymerisationen mit festen Ziegler-Natta-Katalysatoren und verwandten Typen wird oft eine ständige Geschwindigkeitsabnahme beobachtet. In einigen Fällen kann das durch chemische Desaktivierung von katalytisch wirksamen Stellen zustande kommen, in anderen aber ist, wie schon durch eine Reihe von Jahren bekannt, die Ursache ein Einschluss der Katalysatorteilchen und die dadurch bedingte Behinderung der Diffusion des Monomeren zur Katalysatoroberfläche. Eine eingehende und genaue, allgemeine Behandlung ist wegen des Mangels einer Kenntnis der an der Oberfläche und im Inneren der Gelphase bestehenden physikalischen Bedingungen praktisch unmöglich. Gewisse Modellsysteme werden in Betracht gezogen und ihre Anwendbarkeit auf bekannte Fälle diskutiert. In bestimmten Fällen wird ein pseudo-stationärer Zustand der Polymerisationsgeschwindigkeit bei eingekapselten Katalysatorteilchen beobachtet. Die Bedingungen für ein derartiges Verhalten werden überprüft. Analoge Effekte treten in anfangs homogenen, katalytischen Polymerisationen, wie beim Start von Methylmethacrylat mit Grignard-Verbindungen, auf, wenn eine Ausfällung des Polymeren auftritt, da das gefällte Polymere die aktiven Stellen aus der Lösung entfernt.

Discussion

A. D. Caunt (*I.C.I. Ltd., Herts., Great Britain*): Did Dr. Allen observe dark-colored catalyst in the center of colorless capsules of polymer? With polypropylene we do not observe this. The catalyst is completely dispersed throughout growing polymer and is therefore being disrupted into particles of the order below 0.4 size round which polymer grows. For such small catalyst sizes no diffusion control processes can interfere.

The forces causing such a disruption of the $TiCl_3$ are due to enmeshing of polymer molecules growing on the $TiCl_3$ surface in remoter regions when polymer is crystallizing.

P. E. M. Allen: This is most interesting. Dr. Patrick and myself had been speculating about the possibility of the catalyst being torn apart by the swelling of the polymer bound of the surface. There is no evidence that this occurs with our catalysts so indeed gratifying to hear of a case where it does occur.

As far as the question of the rate of polymerization is concerned the criterion is, of course, the monomer concentration at the catalytic sites. If these are still imbedded in the gel then the polymerization must be regarded as physically restricted, though if a diffusion-controlled mechanism is the correct one those fragments near the surface of the capsule of gel will be less restricted than if they had remained attached to the catalyst particle at the center of the capsule.

P. E. M. Allen: There are two points of relevance. These catalysts are capable of polymerizing styrene stereospecifically but only to a relatively small degree. Under the most favorable conditions a 40–50% crystalline polymer may be obtained (see Ref. 5).

There are differences in character in the polymerization in aromatic media, e.g., pure monomer and benzene solution, and non-aromatic media, e.g., *n*-hexane or *n*-heptane solutions, but these differences are slight and certainly no fundamental distinction may be discerned.

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Polymères Optiquement Actifs: Phénomènes d'Autocatalyse dans la Synthèse Asymétrique

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Depuis quelques années, une grande partie des travaux effectués dans notre Institut a eu pour objet la synthèse asymétrique de polymères optiquement actifs, à partir de monomères qui ne contiennent pas d'atomes de carbone asymétriques.[1–3] Ces synthèses asymétriques représentent des cas particuliers, plus avancés, de catalyse stéréospécifique; nous en avons entrepris l'étude pour mieux comprendre non seulement le mécanisme de l'induction asymétrique, mais aussi le mécanisme des polymérisations stéréospécifiques en général.

Des synthèses asymétriques ont été réalisées en présence de catalyseurs anioniques coordonnés, préparés à partir de composés organométalliques contenant des groupes alcoyliques optiquement actifs et aussi à partir de catalyseurs ioniques non asymétriques complexés avec des bases de Lewis optiquement actives. Dans la polymérisation des sorbats alcoyliques à partir de catalyseurs du premier type, on peut penser que l'activité optique soit induite, dans la première unité monomérique, par l'addition du groupe alcoylique asymétrique dérivé du catalyseur et, successivement, transmise le long des chaînes pour un segment plus ou moins long. A partir des catalyseurs du deuxième groupe et à partir des mêmes monomères, l'induction est transmise par la substance complexée à la première unité monomérique sans qu'il y ait formation d'une liaison σ entre l'agent optiquement actif et la chaîne. Même dans ce cas, toutefois, les données expérimentales peuvent être expliquées comme étant dérivées d'une initiation asymétrique et d'un processus de croissance stéréospécifique.

Un cas complètement différent a été rencontré dans la polymérisation asymétrique du benzofuranne; cette polymérisation, dont le comportement a été récemment examiné, est induite par le système catalytique $AlCl_3$–β-phénylalanine.[4]

On a pu préciser que l'induction asymétrique est transmise à la chaîne polymérique par un contreion asymétrique qui, à chaque stade de la polymérisation, favorise l'addition de motifs monomèriques d'un certain signe (D ou L) avec une probabilité différente que celle correspondant aux motifs de signe opposé. Ce type de mécanisme est en accord avec le fait que l'activité optique du polymère est presque indépendente du poids moléculaire. Un autre fait qui a été mis en évidence, concerne la nature des

processus qui diminuent ou arrêtent l'induction asymétrique pendant la réaction: ces processus pourraient être en relation avec les réactions de rupture des chaînes, qui peuvent entraîner le contre-ion, en détruisant l'asymétrie.

D'autres faits n'avaient toutefois pas encore été expliqués. Lors de nombreux essais effectués à partir de concentrations de monomère relativements basses, nous avions observé que le polymère présentait au début une activité optique relativement faible. Cette activité augmente rapidement pendant la polymérisation, elle atteint une valeur maximum et ensuite elle diminue lentement (Tableau I). Tandis que la diminution de l'activité optique spécifique que l'on observe pour les conversions élevées a déjà été en partie clarifiée,[4] le comportement initial, certainement en dehors des incertitudes expérimentales, peur faire penser à un effet d'autocatalyse dans la polymérisation asymétrique. Si cette hypothèse sera confirmée, elle aura un intérêt exceptionnel car cela representerait un cas d'application aux processus chimiques inanimés des règles de sélections, propre au monde des organismes vivants. On pourrait en effet penser qu'au début de la polymérisation le système catalytique ait un pouvoir d'induction asymétrique limité et que ce pouvoir augmente au fur et à mesure que le polymère optiquement actif se forme. En définitive, ce dernier jouerait un rôle essentiel dans l'induction asymétrique.

TABLEAU I

Polymérisations Asymétriques du Benzofuranne en Toluène à −75°C; Catalyseur: $AlCl_3$ (+) Phénylalanine

Essai[a]	W, g polymère / mmoles phénylalanine	$[\alpha]_D$	$W[\alpha]_D$	$\frac{\Delta W[\alpha]_D}{\Delta W}$	$[\eta]$, 100 cc/g
A	1.48	31	46	75	0.85
	2.30	46.7	107	85	0.98
	2.72	52.7	143	85	1.05
B	1.22	50.2	61		0.40
	4.60	76.3	351		0.57
C	0.68	51.5	35	77	0.87
	2.30	69.3	160		1.17

[a] L'essai A a été effectué en ajoutant le monomère au début de la polymérisation, concentration initiale: phénylalanine 2,1 mmoles/l, benzofuranne 125 mmoles/l. Les essais B et C ont été effectués en ajoutant le monomère goutte par goutte au cours de la polymérisation. Essai B concentration initiale: phénylalanine 5,6 mmoles/l. Essai C concentration initial: phénylalanine 5 mmoles/l.

Toutefois, les essais de polymérisation à partir d'un système catalytique symétrique, par ex. $AlCl_3$ ou $AlC_2H_5Cl_2$, ou racémique, par ex. $AlCl_3$ et (±) β-phénylalanine, effectués en présence d'un polymère optiquement actif précédemment préparé, n'ait pas encore fourni de résultats vraiment démonstratifs.

Nous avons alors effectué des essais à partir d'un catalyseur asymétrique optiquement actif en présence d'un polymère préformé, optiquement actif ou non.

Les essais de chaque série ont été effectués en parallèle, en employant la même solution catalytique et en ajoutant dans chaque essai des solutions de polybenzofuranne positif, négatif ou bien racémique. En même temps nous avons effectué des essais comparatifs, en absence de polymère préformé. Les essais experimentals ont été effectués suivant la méthode décrite par Farina et Bressan.[4]

Les données obtenues pour une série d'essais sont reportées dans le Tableau II. Le sens des symboles est analogue à celui que l'on a employé dans un travail précédent:[4] $[\alpha]$ est le pouvoir rotatoir spécifique, mesuré à la lumière du sodium; W représente le poids (en grammes) de polymère par mmole de phénylalanine; les indices i, t, f indiquent respectivement les données relatives au polymère introduit au début de la polymérisation, au polymère total et au polymère formé au cours de la réaction.

TABLEAU II

Polymérisations Asymétriques du Benzofuranne an Toluène à −75°C; Catalyseur: $AlCl_3$–(+)Phénylalanine

Essai[a]	W_i	$[\alpha]_i$	$W_i[\alpha]_i$	W_t	$[\alpha]_t$	$W_t[\alpha]_t$	$[\alpha]_f$	$\frac{\Delta W_t[\alpha]_t}{\Delta W_t}$
D	0.31	+75.3	+23.4	0.627	+79.5	+49.8	+83.5	+92
				0.893	+83	+74.2	+87	
E	0.415	−76.3	−31 7	0.72	−10.1	−7.27	+81	
F	0.386	0	0	0.637	+35	+22.2	+87.5	
G	0	—	—	1.11	+59.5	+66.2	+59.5	+86
				1.42	+65	+92.5	+65	

1 Les essais D-E-F-G- ont été effectués en ajoutant le monom:re goutte par goutte au cours de la polymérisation. L'essai G a été effectué sans addition de polymère avant la polymérisation. Dans les essais D-E-F on a ajouté une quantité W_i de polybenzofuranne ayant activité optique $[\alpha]_i$.

D'après les données reportées, on peut remarquer que l'effet d'autocatalyse ne dépend ni du signe, ni de la valeur de l'activité optique du polymère préexistant. Le polymère formé a un signe optique qui dépend seulement du signe de l'initiateur asymétrique employé (et précisement un signe égal à celui de la phénylalanine) tandis que la valeur de $[\alpha]_f$ est très élevée même à des conversions peu élevées et elle est pratiquement la même dans les nombreux cas que l'on a examinés.

Le phénomène est clairement montré dans la Figure 1, où la dérivé de la fonction $[\alpha]_t W_t$, c'est à dire l'$[\alpha]_f$ instantanné, est représenté par la tangente aux courbes reportées.

Un autre fait intéressant c'est que, par cet examen ou peut très bien encadrer aussi les essais effectués en absence de polymère préformé. Comme il est suggéré par le comportement de la courbe G extrapolée pour des bases valeurs de W, on peut admettre que, après un intervalle de temps

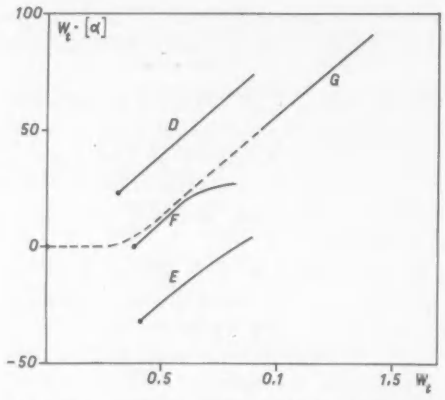


Fig. 1. Variation de $[\alpha]W_t$ en fonction de W_t: (D, E, F) polymérisations effectuées en présence de polymère préformé respecrivement ayant signe positif, négatif et racémique; (G) essai comparatif en absence de polymère préformé. Cocatalyseur: (+) β-phénylalanine

initial pendant lequel il se forme un polymère à activité optique très basse ou même nulle, on ait la formation successive de polymère à pouvoir rotatoir élevé. La constance des vaelurs de $[\alpha]_f$ obtenus dans de nombreux essais (80–90°) fait penser que cette valeur représente la valeur limite de l'activité optique que le polybenzofuranne peut rejoindre avec le système catalytique que nous avons employé; on ne peut d'ailleurs même pas exclure l'hypothèse, que cette valeur soit environ égale à l'activité optique maximum du polybenzofuranne.

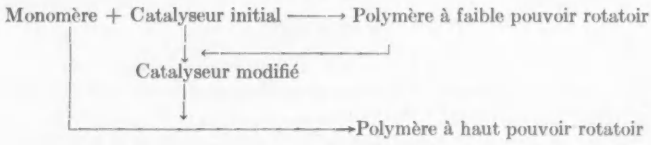
Même si les faits que nous avons observés ne représentent pas le simple phénomène de l'induction asymétrique, on peut toutefois attribuer au polymère une réelle action d'autocatalyse, au sens qu'il exalte l'action stériquement spécifique de la phénylalanine, bien que le signe du pouvoir rotatoir du polymère successivement formé ne dépend que de celle-ci.

D'après l'examen des résultats jusqu'à présent obtenus, on peut affirmer que le phénomène d'autocatalyse ne devrait donc pas être attribué à un effet stérique direct, mais à un effet chimique, dû à la présence du polymère en solution, indépendemment de son signe. Une explication acceptable de ce phénomène peut être donnée par le fait que, à cause de la présence d'atomes d'oxygène étéré, le polybenzofuranne peut se comporter comme une base de Lewis, envers le trichlorure d'aluminium et peut donc modifier la structure du contre-ion.

L'hypothèse d'une modification de l'agent catalytique de la part du polybenzofuranne trouve un autre appuis dans la remarquable différence entre la vitesse de polymérisation relative aux essais effectués en présence de polymère préformé, et les essais de comparaison effectués en son absence:dans ces derniers la vitesse globale est beaucoup plus élevée (de 5 à 10 fois) que celle des premiers types d'essais.

On peut donc penser que le complexe catalytique employé d'ordinaire, ayant un rapport aluminium-phénylalanine (Al/Phe) $\simeq 3$, contient une mole de $AlCl_3$ plus labilement liée ou même libre, mais équilibrée avec celui complexé. Le catalyseur 3:1 aurait une activité élevée en ce qui concerne la vitesse de polymérisation, mais un faible pouvoir d'induction asymétrique, contrairement à ce qui a lieu pour les complexes ayant un rapport inférieur.

Lo schéma formel et hypothétique de la séquence de réaction pourrait être le suivant:


Monomère + Catalyseur initial
Polymère à faible pouvoir rotatoir
Catalyseur modifié
Polymère à haut pouvoir rotatoir

La capacité du polybenzofuranne d'influencer le système qui le produit, et de modifier le pouvoir d'induction asymétrique, peut representer le modèle analogique de l'un des processus possibles qui provoquèrent l'apparition et l'évolution des composés optiquement actifs en nature.

Références

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Résumé

Un phénomène d'autocatalyse a été remarqué dans la polymérisation asymétrique du benzofuranne, effectuée en présence du système catalytique asymétrique $AlCl_3$ et phénylalanine. Dans les expériments effectués à faible concentration de monomère on a remarqué que le polymère obtenu à de basse conversions possède un pouvoir rotatoir mineur que celui obtenu par des conversions plus élevées. Nombreux expériments effectués en présence d'un polymère préformé ont permis d' accerter que le polybenzofuranne a la capacité de réagir avec le système catalytique, en modifiant le pouvoir d'induction asymétrique. Ce fait peut être interprété comme étant un modèle des processus qui ont amené à l'évolution des composés optiquement actifs en nature.

Synopsis

An autocatalytic phenomenon was observed in the curve of the asymetric polymerization of benzofurane, carried out in the presence of an asymetric catalytic system $AlCl_3$-phenylalanine. In experiments carried out at low monomer concentrations the polymer obtained at low degree of conversion shows a rotating power inferior than that for a high yield polymer. Several experiments carried out in the presence of polymer have shown that polybenzofurane reacts with the catalytic system with modifying the asymmetric induction power. This fact can be interpreted as a model of the processes which occur with natural optically active compounds.

Zusammenfassung

Bei der durch das asymmetrische Katalysatorsystem $AlCl_3$-Phenylalanin bewirkten asymmetrischen Polymerisation von Benzofuran wurde ein autokatalytischer Effekt beobachtet. Bei Versuchen mit niedriger Monomerkonzentration besass das bei kleinem Umsatz erhaltene Polymere ein geringeres Drehungsvermögen als das bei höherem Umsatz erhaltene. Zahlreiche Versuche in Gegenwart eines vorgebildeten Polymeren erlaubten die Feststellung, dass das Polybenzofuran die Fähigkeit besitzt mit dem Katalysatorsystem unter Modifizierung des asymmetrischen Induktionsvermögens zu reagieren. Es kann das als ein Modell für die Prozesse aufgefasst werden, die in der Natur zur Entwicklung optisch aktiver Verbindungen geführt haben.

Discussion

Rocaboy: (*1*) Les polymères formés au cours de la polymérisation en présence du prépolymère ont sensiblement la même masse moléculaire que celui-ci. Avez-vous essayé d'isoler les deux polymères?

(*2*) Une réaction avec le prépolymère est-elle exclue au cours de la polymérisation?

M. Farina: (*1*) Le polymère formé a presque le même poids moleculaire que le prépolymère. Dans le cas du polybenzofuranne il n'est pas possible de séparer le prépolymère du polymère formé: on peut penser que cela est possible si l'on emploie un prépolymère avec des propriétés chimiques et physiques différentes de celles du polymère qui se forme.

(*2*) Nous n'avons pas étudié cette question en particulier mais nous pensons que des réactions telles que le greffage n'avaient pas lieu. En effet le poids moléculaire ne montre pas une augmentation telle qu'elle fasse penser à des réactions semblables.

E. Selegny (*Faculté de Nantes, France*): (*1*) Quelles sont les conditions de mesures de pouvoir rotatoire?

(*2*) Quelles observations sont obtenues en dispersion-rotatoire?

(*3a*) Rendement en poids (*3b*) Rendement optique en fonction de la quantité de prépolymère ajoutée?

(*4*) On peut suggérer l'existence d'un nouveau catalyseur optique puisque (*a*) diminue quand (*b*) augmente.

M. Farina: (*1*) Les déterminations du pouvoir rotatoire ont été effectuées à la lumière du sodium, dans le benzène, à la concentration 2–5 o/oo (1 = 4).

(*2*) La courbe ORD du polybenzofuranne a été déterminée en solution dans le dioxanne: elle montre un maximum au dessous de 300 $m\mu$.

(*3*) Nous avons vu que le prépolymère n'a pas un effet stérique direct sur la polymérisation: on obtient les mêmes résultats en employant un prépolymère (+),(−) ou bien racémique. L'effet que nous avons observé est vraiment une modification du système catalytique.

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Stereospecific Polymerization of Aldehydes by Metalloorganic Compounds

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Aldehyde can polymerize by means of organometallic compounds to yield a crystalline, polyether-type polymer. Natta[1] found that the structure of this crystalline polymer is isotactic, and a tentative mechanism of the polymerization was proposed by Furukawa[2] et al. However, the kinetics and the detailed mechanism of this anionic coordinated polymerization reaction have not been obtained, in spite of the importance of stereospecific aldehyde polymerization. In such an anionic coordinated polymerization, the gegen cation has an important role throughout the polymerization reaction, especially in the propagation stage of the reaction as the stereoregulating function. In the course of a study on the effect of catalysts on aldehyde polymerization, we found that the electronegativity and ionic radius of the metal cation of the metalloorganic compounds were related to the stereoregulation of polymerization, the reaction rates R_p and the limit conversion, that is an equilibrium conversion at the final reaction time. As a model monomer, *n*-butyraldehyde was used and the polymerization was carried out in hydrocarbon solvent (*n*-heptane) at −78°C. The following catalysts were used: $B(Et)_3$, $Cd(Et)_2$, $Zn(Et)_2$, $Al(Et)_3$, Grignard reagent, *n*-BuLi, amylNa and metallic K. *n*-Butyraldehyde, responds to K, amylNa, *n*-BuLi, Grignard reagent, $Al(Et)_3$, and $Zn(Et)_2$ but did not polymerize with $B(Et)_3$.

As shown in Figure 1, R_p decreases with increasing electronegativity of the metal in the metalloorganic compounds. In this figure, Li, and Mg denote the metal of *n*-BuLi and EtMgBr, respectively. Of course the organic radical of metalloorganic compounds has an influence on R_p and stereoregularity of polymer, also, but as for alkyl radicals, their effects are much smaller than that of metallic part. The reactions of organo-alkali compounds appear to be too fast from the view point of kinetic study, and moreover the organo-alkali compounds except lithium are insoluble in hydrocarbon solvent such as *n*-heptane. This is why reaction rates of amylNa and K are omitted in Figure 1. The trends of R_p which decrease with increasing electronegativity of the metal, are similar to those of the reaction rates between $\diagdown C{=}O \diagup$ and RM discovered by Gilman.[3] Since

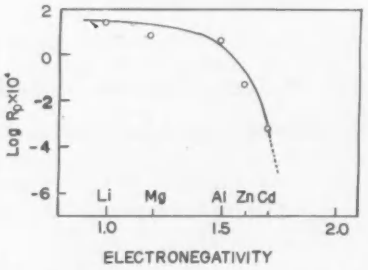


Fig. 1. The relation between logarithmic rate of polymerization and electronegativity of metal cation of organo-metallic compounds.

metalloorganic compounds of Li to B are regarded as covalent compounds of the type $M\overset{+\delta}{-}CH_2\overset{+\delta}{-}R$, the reaction depends upon the partial ionic character of $M\overset{+\delta}{\rightarrow}C$ and $M\overset{+\delta}{\rightarrow}O$—C which is related to the difference in electronegativity of the two atoms. Thus the seat of reactivity of polymerization reaction is the metal cation, as shown in Figure 1.

The equilibrium conversion shows the opposite tendency when compared with Figure 1. The equilibrium conversion is plotted against the electronegativity of the metal cation as shown in Figure 2. The shift of the infrared absorption band arising from $\diagdown C{=}O \diagup$ stretching vibration by coordination with metalloorganics or metal alkoxides is also plotted against the same abscissa in Figure 2. This shift was measured in the following way.

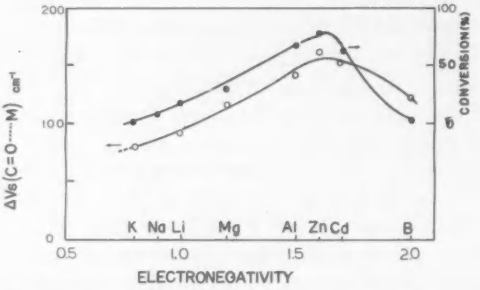
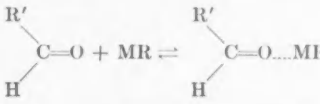
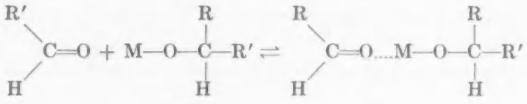


Fig. 2. The relation between the equilibrium conversion and electronegativity of a metal cation of organo-metallic compounds.

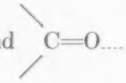
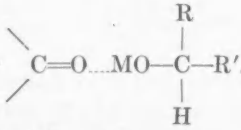
The catalyst was added to the aldehyde solution at room temperature. The polymerization did not proceed at this temperature, because it was far above the ceiling temperature of the polymerization. Thus, coordination between the metalloorganic compound or metal alkoxide and aldehyde as shown in eqs. (1) and (2) occurs; the carbonyl state such as appears as the change in the infrared spectrum of the carbonyl bond, and so its shift was



(1)



(2)

measured from the difference of the bonds between RHC=O and  MR or  . Infrared spectra of various polymers are given in Figs. 3–7, and may be compared with the spectrum of the monomer (Fig. 8). Of particular interest are parallel runs of equilibrium

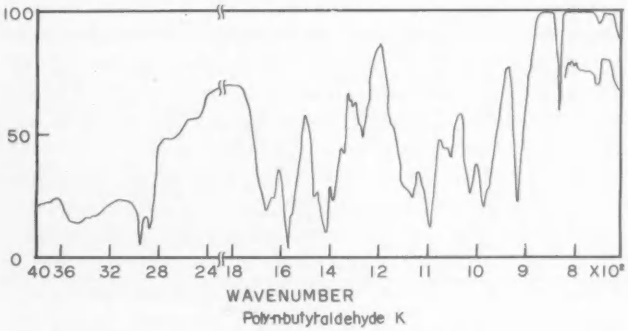


Fig. 3. Infrared absorption spectra of *n*-butyraldehyde monomer.

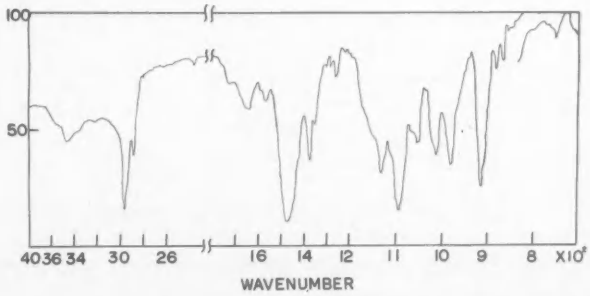


Fig. 4. Infrared absorption spectra of poly-*n*-butylaldehyde polymerized with $Zn(Et)_2$.

conversion and shift of carbonyl bond. The more the shift of $\diagdown\!\!\diagup C{=}O$, the more becomes the equilibrium conversion. This means that the coordinating ability of metal cation to carbonyl oxygen determines the extent

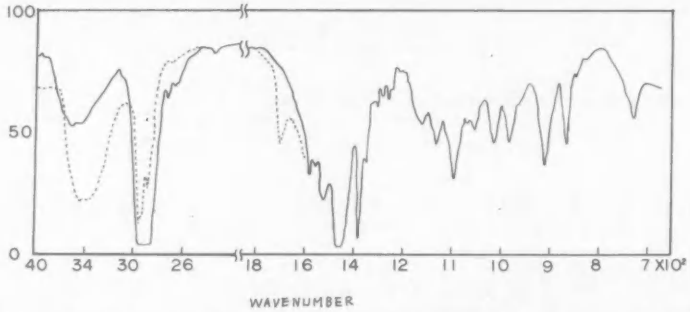


Fig. 5. Infrared absorption spectrum of poly-*n*-butylaldehyde polymerized with Li-*n*-Butyl: (——) by KBr method; (---) by Nojol method.

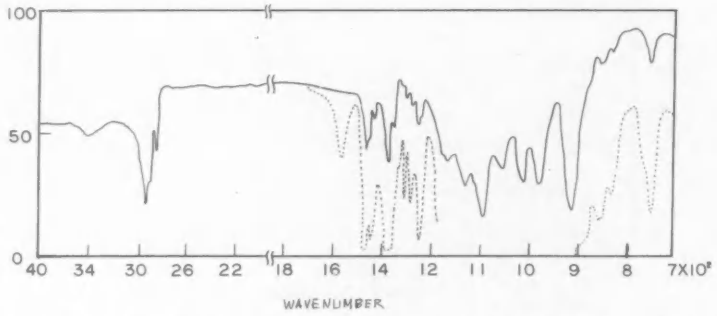


Fig. 6. Infrared spectrum of poly-*n*-butyraldehyde obtained with $Al(Et)_3$ catalyst: (–) film; (——) KBr disk.

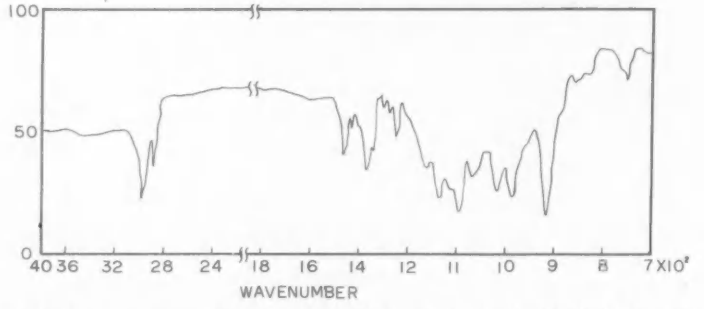


Fig. 7. Infrared spectrum of poly-*n*-butyraldehyde obtained with $Zn(Et)_2$ catalyst.

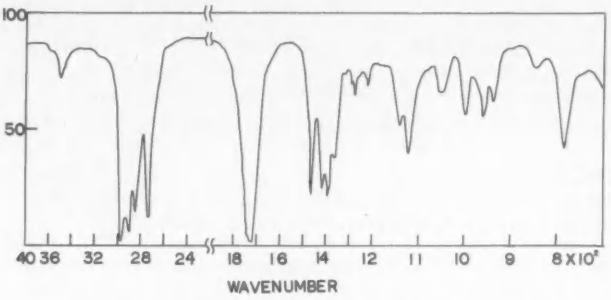


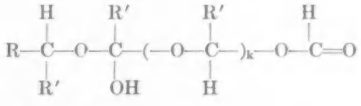
Fig. 8. Infrared spectrum of *n*-butyraldehyde monomer.

of polymerization and at the same time the stereoregularity of the propagation reaction. Group I elements in the periodic table have almost no capacity for coordination, but group II and III elements all possess *p*-orbitals available for coordination and consequently these metals coordinate to

C=O. Among group II and III, group III elements exhibit the greater tendency to coordinate, thus explaining why Al is more effective than Zn or Mg. On the other hand, *n*-butyraldehyde did not form a solid product in the presence of $B(Et)_3$. This is explained as follows. $B(Et)_3$ is strongly coordinating as shown in Figure 2, but the alkoxide $B(Et)_2OR'$ probably does not have such a strong tendency to coordinate because of the highly effective overlaps of the oxygen $2p_z$ orbital with the vacant $2p_z$ orbital of B; thus the initiation step of polymerization cannot take place. Similar results are obtained in the reduction of ketone with metal alkoxide.[4]

The apparent activation energy of each polymerization reaction is very different: −4.2 kcal./mole for reaction with *n*-BuLi − 4.5 kcal./mole for $Al(Et)_3$; +6.2 kcal./mole for $Zn(Et)_2$ in the range of −40 to −78°C. A paper dealing with the kinetics in more detail will be in preparation.

The organo-alkali compounds yield low molecular weight products. These white powders are oligomers rather than polymers, and easily decomposed in air. From the data of Figures 3–5, their structures are assumed to be



where *k* is a small integer. The reaction products with Mg, Al, Zn, and Cd are linear polyether-type polymers and these polymers are highly crystalline, but the degree of stereoregularity of these polymers is not the same. The data of solvent extraction indicate that the stereoregularity of the polymer decreases in the following order with catalysts from Al > Zn > Mg,

Cd. Stereoregularity of the polymer is thus the function of both electronegativity and ionic radius of the metal cation in the catalyst.

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Synopsis

The anionic coordinated polymerization of aldehyde is one of the most interesting stereospecific polymerization reactions recently discovered. However, the kinetic and mechanistic aspects of the stereospecific polymerization of aldehyde remain almost unknown. This report concerns these aspects of aldehyde polymerization. The catalysts used in this study are organometallic compounds such as $B(Et)_3$, $Cd(Et)_2$ $Zn(Et)_2$, Grignard reagent, *n*-BuLi, amylNa, and metallic K. In many cases *n*-butyraldehyde was used as a model monomer and the polymerization was carried out at low temperatures (-78 to -40°C.) in hydrocarbon solvent. This monomer responds to K, amylNa, *n*-BuLi, Grignard reagent, $Al(Et)_3$, $Zn(Et)_2$, and $Cd(Et)_2$, but does not yield polymer with $B(Et)_3$. Grignard reagent, $Al(Et)_3$, and $Zn(Et)_2$ are powerful catalysts for the stereospecific polymerization, whereas organometallic compounds of alkali metals give generally low molecular weight products. The reaction velocity R_p and the limit conversion, that is, equilibrium conversion, are related to the electronegativity of the metal cation in organometallic compounds. The shift of infrared absorption band arising from the C=O stretching vibration by coordination of organometallics (C=O---MR) is also parallel to the relation between electronegativity and equilibrium conversion. The kinetics of polymerization with *n*-BuLi, secBuMgBr, $Al(Et)_3$, $Zn(Et)_2$ were investigated and the velocity of polymerization reactions is expressed in terms of monomer and catalyst concentration. The apparent activation energy of the reaction is -4.9 kcal./mole for the reaction with LiBu *n*-BuLi, -4.5 kcal./mole for $Al(Et)_3$, and 6.2 kcal./mole for $Zn(Et)_2$. The polymerization reaction depends on the dielectric constant of the polymerization medium. If the monomer concentration is low, R_p is expressed by a relation of the form $\log R_p = A + B/D$ where A and B are constant, and D is the dielectric constant of the solvent. The solvent was varied from *n*-heptane to methyl isobutyl ketone. The stereoregularity of the polymer also decreases with increasing dielectric constant of solvent. On the basis of these results, we propose a mechanism of stereospecific polymerization of aldehyde.

Résumé

La polymérisation anionique de coordination de l'aldéhyde est un des cas les plus intéressants parmi les polymérisations stéréospécifiques récemment découvertes, mais la cinétique et le mécanisme de cette réaction restent toujours peu connus. Ce rapport a trait aux différents aspects de cette polymérisation. On utilise comme catalyseur des dérivés organométalliques, comme le $B(Et_3)$, $Cd(Et)_2$, $Zn(Et)_2$, le réactif de Grignard, *n*BuLi, AmylNa, ainsi que le potassium métallique. Dans plusieurs cas le *n*-butyraldéhyde sert comme monomère modèle et on effectue la polymérisation à basse température (-78 à -40°) dans des solvants hydrocarbonés. L'aldéhyde polymérise avec le potassium, l'amylNa, le *n*-butyl-Li, le réactif de Grignard, $Al(Et)_3$, $Zn(Et)_2$ et $Cd(Et)_2$, mais il ne se forme pas de polymère avec le $B(Et)_3$. Le réactif de Grignard, $Al(Et)_3$ et $Zn(Et)_2$ sont des catalyseurs énergiques pour la polymérisation stéréospécifique, tandis que les dérivés organométalliques des métaux alcalins donnent généralement des produits de bas poids moléculaire. La vitesse de la réaction R_p et la conversion limite, c.à.d.

la conversion à l'équilibre, sont reliées à l'électronégativité du cation des composés organométalliques. Le déplacement de la bande d'absorption infra-rouge résultant de la vibration d'élongation du C=O provoquée par la coordination avec les organométalliques (C=O...MR), peut être mis en parallèle avec la relation entre l'électronégativité et la conversion à l'equilibre. On a étudié la cinétique de la polymérisation avec le *n*-BuLi, le sec. BuMgBr, l'$Al(Et)_3$ et le $Zn(Et)_2$, et on a exprimé les vitesses de polymérisation en termes de concentration en monomère et en catalyseur. L'énergie d'activation apparente de la réaction est de 4.9 kcal/mole pour la réaction avec le *n*-BuLi, 4.5 kcal/mole pour le $Al(Et)_3$ et 6.3 kcal/mole pour le $Zn(Et)_2$. La polymérisation dépend aussi de la constante diélectrique du milieu. Si la concentration en monomère est faible, R_p suit la relation suivante $\log R_p = A + B/D$ dans laquelle A et B sont des constantes et D est la constante diélectrique du solvant. La nature du solvant change du *n*-heptane à la méthyle-isobutyle-cétone. La stéréospécificité du polymère diminue aussi avec une augmentation de la constante diélectrique. Considérant ces résultats, on propose un mécanisme pour la polymérisation stéréospécifique de l'aldéhyde.

Zusammenfassung

Die anionisch-koordinative Polymerisation von Aldehyden ist eine der interessantesten der in letzter Zeit entdeckten stereospezifischen Polymerisationsreaktionen. Uber Kinetik und Mechanismus der stereospezifischen Aldehydpolymerisation ist jedoch kaum Näheres bekannt. Die vorliegende Arbeit betasst sich mit der Polymerisation von Aldehyden. Als Katalysatoren wurden bei diesen Untersuchungen organometallische Verbindungen wie $B(Et)_3$, $Cd(Et)_2$, $Zn(Et)_2$, Grignardverbindungen, *n*-BuLi, AmylNa, und metallisches K verwendet. In vielen Fällen wurde *n*-Butyraldehyd als Modell-Monomeres verwendet und die Polymerisation bei niedrigen Temperaturen (−78° bis 40°C) in Kohlenwasserstoffen als Lösungsmittel durchgeführt. Dieses Monomere polymerisiert mit K, AmylNa, *n*-BuLi, Grignardverbindungen, $Al(Et)_3$, $Zn(Et)_2$, und $Cd(Et)_2$, liefert aber mit $B(Et)_3$ kein Polymeres. Während Grignardverbindungen, $Al(Et)_3$ und $Zn(Et)_2$, wirksame Katalysatoren für die stereospezifische Polymerisation sind, führt die Verwendung von organometallischen Verbindungen der Alkalimetalle im allgemeinen zu Produkten niedrigen Molekulargewichts. Die Reaktionsgeschwindigkeit R_p und der Grenzumsatz (Gleichgewichtsumsatz) stehen zur Elektronegativität des metallkations in den organometallischen Verbindungen in Beziehung. Die Verschieburg der auf die C=O-Valenzschwingung zurückgehende Infrarot-Absorptionsbande durch Koordination mit den organometallischen Verbindungen (C=O...MR) verläuft der Beziehung zwischen Elektronegativität und Gleichgewichtsumsatz parallel. Es wurde die Kinetik der Polymerisation mit *n*-BuLi, sek-Bu Mg Br, $Al(Et)_3$ und $Zn(Et)_2$ untersucht und die Polymerisationsgeschwindigkeit als Funktion der Monomer- und Katalysator-Konzentration dargestellt. Die scheinbare Aktivierungsenergie ist −4,9 kcal/Mol für reaktion mit *n*-BuLi, und 4,5 kcal/Mol $Al(Et)_3$ und 6,2 kcal/Mol für $Zn(Et)_2$. Die Polymerisation wird durch die Dielektrizitätskonstante des Polymerisationsmediums beeinflusst. Bei niedriger Monomerkonzentration kann R_p durch eine Beziehung des Typs $\log R_p = A + B/D$ ausgedrückt werden, wobei A und B Konstanten und D die Dielektrizitätskonstante des Mediums ist. Das Lösungsmittel wurde durch den Übergang von *n*-Heptan zu Methylisobutylketon variiert. Die Stereospezifität des Polymeren nimmt ebenfalls mit steigender Dielektrizitätskonstante des Lösungsmittels ab. Auf der Basis dieser Ergebnisse wurde ein Mechanismus für die stereospezifische Polymerisation von Aldehyden vorgeschlagen.

Discussion

R. O. Colclough (*Manchester University, Great Britain*): The relative inactivity of $B(Et)_3$ is not surprising in view of the fact that even BF_3 is a weaker electron-acceptor than $Al(Me)_3$, to judge by the heat of addition of dimethyl ether to BF_3 in the gas phase

which is some 5 kcal/mole lower than the corresponding heat of addition to $Al(Me)_3$. If the formation of $(Et)_2BOR$ is assumed, it would be necessary to attribute its lack of coordinating power to back-donation of electrons from the oxygen only if it is monomeric in solution, since the formation of a stable dimeric complex would account for the observed inactivity.

It is stated that the velocity of polymerization has been expressed in terms of monomer and catalyst concentrations. How is the reaction velocity R_p defined, and how does it vary with monomer and catalyst concentrations?

H. Sobue: The effects of monomer and catalyst concentration on the polymerization rate R_p were examined; and we find that R_p is proportionally increased with the catalyst concentration C in it low concentration, but the increase of rate stop in a range beyond some concentration and finally the rate reach to an equilibrium value or the rate decrease in higher concentration. This phenomena is illustrated by the view of catalyst's association and the following mechanism of polymerization.

In the case of polymerization with LiBn, the mechanism is considered as follows:

$$(\mathrm{LiBn})_n \rightleftarrows n\ \mathrm{LiBn}$$

$$\mathrm{BnLi} + \mathrm{M} \xrightarrow{ki} \mathrm{BnLi}$$

$$\mathrm{BnLi}^+ + \mathrm{M} \xrightarrow{k_p} \mathrm{BnM_2Li^*}$$

$$\mathrm{BnMrLi} + \mathrm{M} \xrightarrow{k_p} \mathrm{BnMr} + \mathrm{1Li^*}$$

$$\mathrm{BnMrLi^*} + \mathrm{M} \xrightarrow{kt_1} \mathrm{BnMr} + \mathrm{LiM}$$

$$\mathrm{BnMrLi^*} \xrightarrow{kt_2} \mathrm{BnMr_2Li}$$

$$R_p = -\frac{d[\mathrm{M}]}{dt} = \frac{ki[\mathrm{M}]^2\,[\mathrm{BnLi}]}{kt_2(1 + kt_1/kt_2\,[\mathrm{M}])}$$

On the case of $[\mathrm{LiBn}]^n/[(\mathrm{LiBn})]_n = k$

$$n \fallingdotseq 7 \qquad K \fallingdotseq 10^{-11\sim10}$$

$$[\mathrm{Li}]_0 \sim 0.05\ \mathrm{mol/L}$$

The effective concentration of LiBn reaches a constant value. On the case of $[\mathrm{Li}]_0 < 0.05$ mol/L

$$\mathrm{LiBn} \sim \mathrm{Li_0}$$

The experimental equation is as follows: $R_p = k[\mathrm{M}]^2\,[\mathrm{C}]$ in the case of

$$[\mathrm{C}] \leqslant 0.05\ \mathrm{mol/L}$$

$$[\mathrm{M}] \leqslant 4\ \mathrm{mol/L}$$

$R_p = k[\mathrm{M}]^2$ in the case of $[\mathrm{C}] > 0.05$ mol/L and

$$1/\bar{P} = kt_1/k_p + (Kt_2/k_p)\,(1/[M])$$

$[M]$: monomer concentration

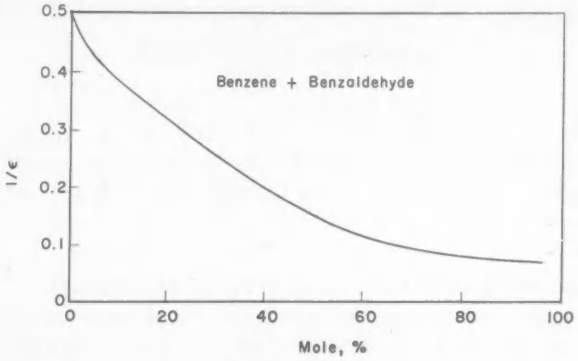
In the case of polymerization with Grignard reagent,

$$R_p = K[\mathrm{M}][\mathrm{C}]^2$$

R. O. Colclough: Does the order in monomer take into account the effect of monomer concentration on the dielectric constant?

H. Sobue: R_p is increased with increasing of [M] in low concentration, but the rate reaches a maximum value with increasing of [M], and finally the rate decrease with [M].

The effect of [M] on R_p is illustrated from dielectric constant of the system. For example in a mixture of benzaldehyde and benzene. The ϵ of the system varies as following figure.



Discussion Fig. 1.

D: Dielectric constant

$$D = \left(\frac{\epsilon - 1}{\epsilon - 2}\right)\left(\frac{M}{d}\right)$$

R. O. Colclough: What is the estimated value of the ceiling temperature and values of ΔH and ΔS for polymerization?

H. Sobue: We did not yet determine the accurate ceiling temperature and value for ΔH and ΔS, but it is obvious that the ceiling temperature exist between room temperature to $-40°C$.

We wish to report in near future our papers concerning stereospecific propagation, assuming that the stereospecificity of polymer is decided by a probability ratio of isotactic addition and syndiotactic addition β/α, that is, velocity ratio of isotactic propagation and syndiotactic propagation K_s/K_i, this ratio is connected with the differences of entropy and enthalpy $\Delta S^{\ddagger}$ $\Delta H^{\ddagger}$ as follows

$$\beta/\alpha = K_s/K_i = \exp\{\Delta S^{\ddagger}/R - (\Delta H^{\ddagger}/RT)\}$$

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A Kinetic Investigation of the Formation of Amorphous and Crystalline Polyethylidene from the Gold-Catalyzed Decomposition of Diazoethane in Ethyl Ether Solutions

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Some years ago, Saini and Nasini[1] showed that when a few drops of an ethyl ether solution of $AuCl_3$ is added to an ethereal solution of diazoethane, there is a reduction of the gold salt to colloidal gold, and the diazoalkane decomposes with nitrogen evolution. As the reaction goes on, blue flakes of crystalline polyethylidene surrounding gold particles separate from the liquid. By dropping the reaction liquid in an excess of methanol, the amorphous polyethylidene is precipitated. The yield of crystalline polyethylidene, which is only soluble in hot solvents such as hot xylene and hot α-chloronaphthalene is about 5%. The yield of the cold ethyl ether-soluble amorphous polyethylidene is about 35%.

Further investigations lead to the conclusion that the catalytic activity in decomposing diazoethane with polyethylidene formation is essentially due to the colloidal gold arising from the reduction of the gold salt used as a primary catalyst, as shown by electron microscopy[2] and by the fact that gold films prepared by evaporating gold metal under high vacuum decompose diazoethane dissolved in ethyl ether, and amorphous ethyl ether-soluble polyethylidene together with small amounts of the crystalline product are formed.[2,3]

Further researches upon the catalytic activity of metal films towards polyethylidene formation from the decomposition products of diazoethane,[3] as well as the results of an investigation on the low molecular weight products which are formed together with the polymeric materials in the course of the reaction,[4] lead to the formulation of some working hypotheses about the path of the reactions giving polyalkylidenes from the metal-catalyzed decomposition of diazoalkanes.[4,5]

With the aim of better understanding the mechanism of this kind of polymer formation reactions, a kinetic investigation of polyethylidene formation from the decomposition of diazoethane dissolved in ethyl ether, using $AuCl_3$ as primary catalyst, was then undertaken, and the main results so far obtained are presented and discussed here.

RESULTS

Rates of Formation of Amorphous and Crystalline Polyethylidene

The course of the reaction was followed by weighing the polymers formed at different times. The full experimental details will be reported elsewhere.[6]

The experiments were carried out in a temperature range between about -30 and $+20$°C. with different concentrations of either the catalyst or diazoethane. Since poorly reproducible results are obtained when concentrated solutions of diazoethane are used, our experiments are concerned only with dilute diazoethane solutions in ethyl ether, namely for a concentration range of about 4×10^{-2}–3×10^{-1} mole/l.

As shown in Figure 1, the rates of formation of both amorphous (cold ethyl ether-soluble) polyethylidene and crystalline (insoluble in the reaction medium) polyethylidene from the gold-catalyzed decomposition of ethyl ether solutions of diazoethane depend on the first power of the catalyst concentration. This result is in agreement with what was already reported by Saini et al.[7] in the case of the formation of polymethylene from the decomposition of diazomethane dissolved in ethyl ether using gold as a catalyst.

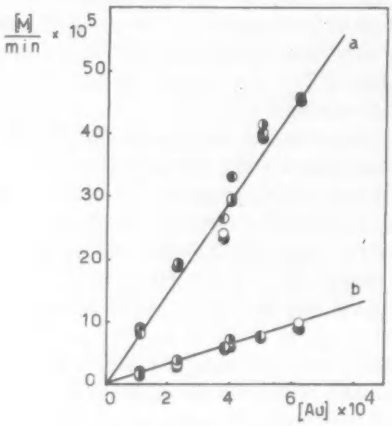

Fig. 1. Dependence of the rates of formation (groundmole/l.) of amorphous (*a*) and crystalline (*b*) polyethylidene upon catalyst concentration (g. atoms of gold/l.) at various diazoethane concentrations: (○) 1.35×10^{-1} mole/l.; (●) 1.60×10^{-1} mole/l.; (◑) 1.75×10^{-1} mole/l.; (◐) 3.10×10^{-1} mole/l. Temperature of reaction: 0°C.

The rate of formation of either amorphous or crystalline polyethylidene has been found to be practically independent upon diazoethane concentration, almost in the range of the diazoethane concentrations of the present investigation, as it is easy to see from the Figures 2 and 3. It is to be pointed

out at this regard, that also the rate of decomposition of diazoethane does not depend upon diazoethane concentration for the system under investigation,[6] in agreement with the result already reported by Ledwith[8] for the decomposition of diazoethane solutions in tetrahydrofuran using $AuCl_3$ as a catalyst.

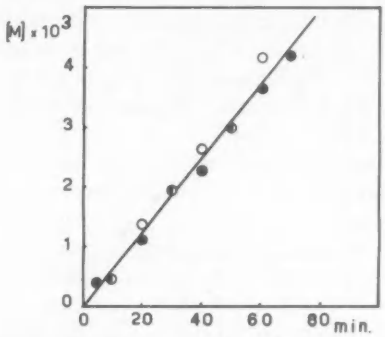

Fig. 2. Rate of formation of crystalline polyethylidene (groundmole/l.) against time of reaction at various diazoethane concentrations: (○) 2.17×10^{-1} mole/l.; (●) 1.22×10^{-1} mole/l.; (◐) 0.35×10^{-1} mole/l. Temperature of reaction: 0°C.; catalyst concentration: 5.1×10^{-4} g. atoms/l. of gold.

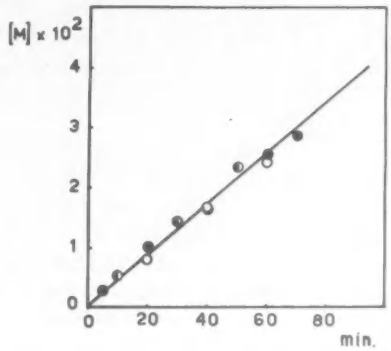

Fig. 3. Rate of formation of amorphous polyethylidene (groundmole/l.) against time of reaction at various diazoethane concentrations: (○) 2.17×10^{-1} mole/l.; (●) 1.22×10^{-1} mole/l.; (◐) 0.35×10^{-1} mole/l. Temperature of reaction: 0°C.; catalyst concentration: 5.1×10^{-4} g. atoms/l. of gold.

Temperature Dependence of the Rates of Polyethylidene Formation

The rates of both amorphous and crystalline polyethylidene formation decrease as the temperature of reaction is lowered. The experimental data fit well on an Arrhenius plot (see Fig. 4), and apparent energies of activation of about 12 kcal./mole and 8 kcal./mole have been calculated for the

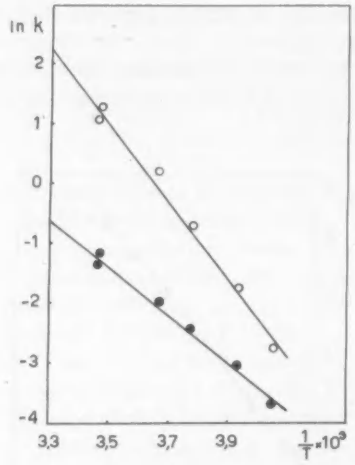

Fig. 4. Arrhenius plot showing the dependence of the rate constants (groundmole/l./min.) of formation of amorphous (O) and crystalline (●) polyethylidene upon temperature.

processes giving rise to amorphous and crystalline polyethylidene, respectively. The value of the apparent energy of activation for the formation of amorphous polyethylidene does not greatly differ from that calculated by Saini et al.[7] in the case of the gold-catalyzed decomposition of diazomethane dissolved in ethyl ether and can be compared with the value already reported by Bawn and Rhodes[9] for the same system when copper stearate is used as a catalyst.

Since polymethylene is formed in nearly quantitative yields from the decomposition of diazomethane dissolved in ethyl ether with either gold or copper stearate as catalysts, the above quoted energies of activation might be regarded as those of polymer formation. In fact it has been observed from our experiments[6] that the apparent activation energy for the decomposition of diazoethane in ethyl ether solutions using gold as a catalyst does not greatly differ from that of the process of formation of amorphous polyethylidene.

The relative yield of crystalline polyethylidene increases as the temperature of reaction is lowered, as a consequence of the fact that the apparent activation energy for this process is lower than that for the formation of the amorphous product, and it has been found that it practically equals that of amorphous polyethylidene when the reaction is carried out at about -50°C. This result is not surprising if it is taken into account that from free radical polymerizations carried out at very low temperatures, polymers are obtained having a higher degree of crystallinity and stereoregularity than those prepared by the same reaction at room temperature.[10] Either the experimental data[11] or the theoretical calculations[12] show that in these

cases a syndiotactic replacement is predominant. As has already been reported,[5] a syndiotactic chain fully extended on the plane seems to be the most probable configuration of crystalline polyethylidene.

Degree of Polymerization of Amorphous Polyethylidene

The number-average degree of polymerization of amorphous polyethylidenes prepared from the gold-catalyzed decomposition of ethyl ether solutions of diazoethane under different experimental conditions, have been measured by means of an ebulliometer similar to the one already described by Ray.[13] The full experimental details will be reported in a forthcoming paper.[14]

The degree of polymerization of the amorphous polyethylidenes prepared under the same experimental conditions of the kinetic measurements is low and does not exceed 100. The number-average degree of polymerization of some crystalline polyethylidenes has also been measured, and it has been found to be larger than that of the amorphous polymer formed in the same run. By carrying out the reaction at low temperatures, crystalline polyethylidenes having a number-average degree of polymerization as high as about 300 have been obtained. It is however to be pointed out that amorphous polyethylidenes having a number-average degree of polymerization of about 700 have been prepared from the decomposition of ethyl ether solutions of diazoethane by using, for instance, films of tungsten as catalysts. So the catalytic system seems to be of some importance for the obtention of high molecular weight polyalkylidenes.

In Figures 5 and 6 the reciprocal of the number-average degree of polymerization of the amorphous polyethylidenes prepared at 0°C. has been plotted against catalyst concentration and against the initial diazoethane concentration, respectively, and it can be seen that the degree of polymerization of amorphous polyethylidene decreases with an increase of either the initial concentration of diazoethane or the concentration of the catalyst.

The degree of polymerization of amorphous polyethylidene increases with

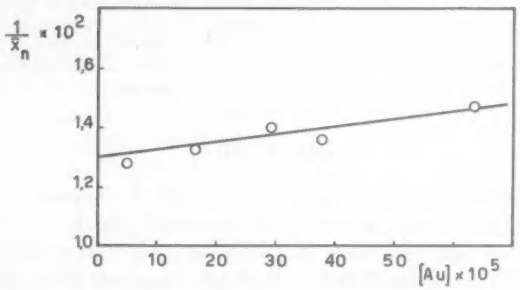

Fig. 5. Dependence of the number-average degree of polymerization of amorphous polyethylidene on gold concentration (g. atom/l.). Temperature of reaction: 0°C.; initial diazoethane concentration: 2.5×10^{-1} mole/l.

decreasing temperature of reaction, as seen from Figure 7, as usually observed in polymer chemistry.

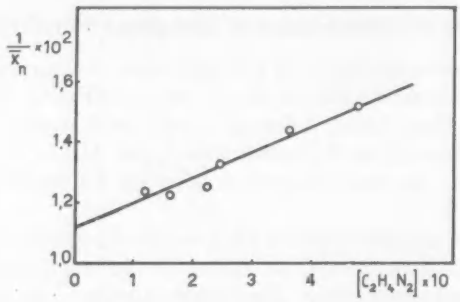

Fig. 6. Dependence of the number-average degree of polymerization of amorphous polyethylidene on initial diazoethane concentration (mole/l.). Temperature of reaction: 0°C.; gold concentration: 1.7×10^{-4} g. atom/l.

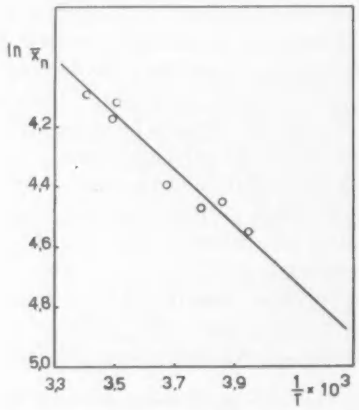

Fig. 7. Dependence of the number-average degree of polymerization of amorphous polyethylidene upon temperature of reaction (°K). Initial diazoethane concentration: 1.90×10^{-1} mole/l.; gold concentration: 1.7×10^{-4} g. atom/l.

DISCUSSION

As already reported,[5,7] in the gold-catalyzed decomposition of diazoalkanes the fraction of the polyalkylidene insoluble in the reaction medium (in the present case crystalline polyethylidene) acts as a protective agent for the colloidal particles of gold arising from the reduction of the gold halide used as primary catalyst and prevents them from aggregating. Crystalline polyethylidene occluding colloidal gold, when put in contact with a fresh solution of diazoethane, catalyzes further polymer formation, and there is

evidence that, as in the case of polymethylene,[7] each active center of the gold surface which initiates either an amorphous or a crystalline polyethylidene chain retains practically unaltered its ability to form macromolecules, independently of the number of polyalkylidene chains produced.

The rates of both amorphous and crystalline polyethylidene formation have been found to be practically independent upon diazoethane concentration. It is well known that, when a substance undergoing decomposition is also strongly adsorbed on the catalyst, the active centers of the catalyst are practically saturated, and an apparent zero order for the reaction will be observed.

Saini et al.[7] reported for the formation of polymethylene from the decomposition of diazomethane in ethyl ether catalyzed by gold an apparent first-order reaction upon the concentration of the diazoalkane. It is, however, to be pointed out that, as shown from electron microscopy,[2] the colloidal particles of gold arising from the reduction of $AuCl_3$ by diazoethane are larger than those obtained when diazomethane is used. In addition, it is to be taken into account that, as generally observed, the adsorption for the first terms of an homologous series increases with increasing molecular weight. Both these factors might be taken to explain either the difference in the kinetic behavior of diazomethane and of diazoethane towards gold catalyst or why the rates of the processes of polyethylidene formation as well as of diazoethane decomposition, at a given temperature of reaction, depend only upon the amount of the catalyst, and then upon the total surface at disposal.

Up to the present time, only gold, among the metals active in promoting polyethylidene formation from the decomposition products of diazoethane, has been found to be endowed with a stereoregulating activity.[3] The difference between the activation energies of the processes leading to amorphous and crystalline polyethylidene might suggest two different reactions, both catalyzed by gold, taking place at the same time with the same kinetic behavior and leading to the same polymeric products, of which one is amorphous and the other shows a stereoregular arrangement of the substituents along the chain. It might be tentatively suggested that crystalline polyethylidene would be formed only on the surface of the gold particles through the addition to the growing polymer chain of ethylidene fragments or of diazoethane molecules adsorbed on neighboring sites of the catalyst. A mechanism of this kind would, of course, be characterized by a low value of the activation energy.

By comparing the slopes of the lines of Figures 5 and 6, it appears that, at a given temperature of reaction, the most important factor controlling the degree of polymerization of amorphous polyethylidene prepared under the experimental conditions of the present investigation is the initial concentration of diazoethane. Since the rate of amorphous polyethylidene formation, as well as that of diazoethane decomposition, does not depend upon diazoethane concentration, it might be suggested that chain transfer reactions with diazoethane could be of some importance as chain termina-

tion processes. It is however to be pointed out that, since the molecular weight measurements were carried out on polyethylidenes prepared by allowing the reaction to go to the completion, to get a quantitative evaluation of the experimental results, it is necessary to take into account the degree of conversion of diazoethane to polyethylidene and the molecular weight distribution in the polymers. Work is in progress on this point and it will be reported in the near future.

The authors wish to express their gratitude to Prof. A. G. Nasini for most helpful discussions and to Aeronautical Systems Division, AFSC, which has sponsored part of this work through the European Office, Office of Aerospace Research, United States Air Force, under Contract AF 61 (052)-708.

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11. See, for instance, J. D. Stroupe and R. E. Hughes, *J. Am. Chem. Soc.*, **80**, 2341 (1958); R. G. J. Miller, B. Mills, P. A. Small, A. Turner-Jones, and D. G. M. Wood, *Chem. Ind. (London)*, **1958**, 1323; B. S. Garrett, W. E. Goode, S. Gratch, J. F. Kincaid, C. L. Levesque, A. Spell, J. D. Stroupe, and W. H. Watanabe, *J. Am. Chem. Soc.*, **81**, 1007 (1959).
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Synopsis

The kinetics of both amorphous and crystalline polyethylidene formation from the gold-catalyzed decomposition of diazoethane in ethyl ether solutions has been investigated. The results show that the rate of both amorphous and crystalline polyethylidene formation is proportional to the first power of the catalyst concentration and does not depend upon diazoethane concentration in the range between 4×10^{-2} and 3×10^{-1} moles/l. Apparent energies of activation of 12 and 8.0 kcal./mole have been calculated for the processes leading to amorphous polyethylidene and to crystalline polyethylidene, respectively. The degree of polymerization of the amorphous polyethylidene obtained from the gold-catalyzed decomposition of ethyl ether solutions of diazoethane decreases with increasing temperature of reaction as well as with increasing concentration of the catalyst and of diazoethane. On the basis of the experimental results, some hypotheses for the mechanism of the reactions leading to amorphous and crystalline polyalkylidenes from the metal-catalyzed decompositions of diazoalkanes are drawn.

Résumé

On a étudié la cinétique de formation du polyéthylidène cristallin et amorphe par la décomposition, catalysée par l'or, des solutions de diazoéthane dans l'éther éthylique. Les résultats montrent que la vitesse de formation des polyéthylidène est proportionnelle à la première puissance de la concentration en catalyseur. La vitesse ne dépend pas de la concentration en diazoéthane dans le domaine de 4×10^{-2} et 3×10^{-1} mole/l. L'énergie d'activation apparente de 12 et de 8.0 kcal/mole est calculée tant pour le processus qui fournit le polyéthylidène amorphe que celui qui fournit le polyéthylidène cristallin. Le degré de polymérisation du polyéthylidène amorphe obtenu par la décomposition, des solutions de diazoéthane dans l'éther éthylique catalysée par l'or diminue avec l'augmentation de la température de la réaction et avec l'augmentation de la concentration du catalyseur et en diazoéthane. Sur la base de ces résultats expérimentaux, on propose des hypothèses concernant le mécanisme des réactions qui conduisent aux polyalcoylidènes cristallins et amorphes par la décomposition du diazoéthane catalysée par un métal.

Zusammenfassung

Die Kinetik der Bildung von amorphen und kristallinem Polyäthyliden bei der durch Gold katalysierten Zersetzung von Diazoäthan in Äthylätherlösung wurde untersucht. Die Ergebnisse zeigen, dass die Geschwindigkeit der Bildung sowohl von amorphem als auch kristallinem Polyäthyliden der Katalysatorkonzentration direkt proportional und von der Diazoäthankonzentration im Bereich von 4×10^{-2} bis 3×10^{-1} mol/l unabhängig ist. Für den zum amorphen und den zum kristallinen Polyäthyliden führenden Vorgang wurde eine scheinbare Aktivierungsenergie von 12 bzw. 8,0 kcal/Mol berechnet. Der Polymerisationsgrad des amorphen, bei der obigen Reaktion erhaltenen Polyäthylidens nimmt mit steigender Reaktionstemperatur und mit steigender Katalysator- und Diazoäthankonzentration ab. Auf der Basis der Versuchsergebnisse werden einige Hypothesen betreffend den Mechanismus der bei der metall-katalysierten Zersetzung von Diazoalkanen zu amorphen und kristallinen Polyalkylidenen führenden Reaktionen aufgestellt.

Discussion

J. J. M. Evers (*Staatsmijnen in Lumburg, Lab. Central, Gekeen, Hollande*): Est-ce l'auteur a trouvé de l'hydrogène (produit de réaction)?

L. Trossarelli: Pas du tout.

K. Veselý (*Institut de Chimie Macromoléculaire, Brno, Tchécoslovaquie*): L'existence de deux liaisons doubles dans chaque macromolécule peut être expliquée par la réaction du transfert avec le monomère et par la réaction de réamorçage. L'existence de la réaction d'amorçage, formulée par l'auteur est improbable.

JOURNAL OF POLYMER SCIENCE: PART C NO. 4, PP. 167–171

Recent Progress in the Mechanism of the Formation of Polyethylidene from Diazoethane

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In a previous paper[1] the main results of a kinetic investigation on the formation of both amorphous and crystalline polyethylidene from the decomposition products of diazoethane were reported and discussed, chiefly as concerns the overall catalytic action of metallic gold towards the decomposition of diazoalkanes with formation of both amorphous and crystalline polyalkylidenes.

In the present paper the results from such a kinetic investigation, as well as those so far obtained from research upon the chemical structure of the polyethylidene chain, will be discussed, reference being made to some of the working hypotheses previously formulated about the mechanism of this kind of polymer formation reactions.[2–4] It will be shown that, on the basis of all the experimental evidence, a suitable mechanism for the reactions leading to amorphous and crystalline polyethylidene from the gold-catalyzed decomposition of diazoethane might be proposed. It is, however, to be pointed out that the present mechanism could easily be extended to the more general problem of polyalkylidene formation from the decomposition of diazoalkanes when metals are used as catalysts.

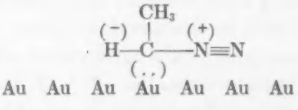
It is now well known[3,5,6] that when a few drops of a dilute solution of a gold halide in ethyl ether is added to a solution of diazoethane in the same solvent, the gold salt is reduced, the diazoalkane decomposes with evolution of nitrogen, and blue flakes of crystalline polyethylidene separate from the liquid. From the reaction liquid the amorphous polyethylidene can be precipitated by dropping it in a large excess of methanol. As in the case of polymethylene formation from the decomposition of diazomethane catalyzed by gold halides,[6] the crystalline polyethylidene occluding colloidal gold (this polymer, insoluble in the reaction medium acts as a protective agent for the colloidal gold particles and prevents them from aggregating) acts as a catalyst for further polymer formation, and there is evidence that the true catalyst is the gold metal and that the catalyst retains practically unaltered its ability to form both crystalline and amorphous polyethylidene chains, independently of the number of macromolecules produced.

The yield of crystalline polyethylidene from the gold-catalyzed de-

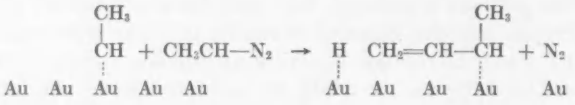
composition of diazoethane is about 5% and that of the amorphous product is about 35%. In the course of the reaction, other hydrocarbon products are formed, and by gas chromatographic analysis it has been shown that they are essentially a mixture of *cis*-butene-2 and of *trans*-butene-2 in nearly equal amounts together with small quantities of ethylene and ethane.[2]

The rates of both amorphous and crystalline polyethylidene formation from the decomposition of diazoethane in ethyl ether solutions with gold as a catalyst has been found to be independent of diazoethane concentration and to increase linearly with increasing catalyst concentration.[1,7] The same kinetic behavior has been observed for the reaction of diazoethane decomposition. The apparent energies of activation for the processes leading to amorphous and crystalline polyethylidene have been calculated to be about 12 kcal./mole and 8 kcal./mole.[1,7] The apparent activation energy for the decomposition of diazoethane is close to 14 kcal./mole.[7]

We might suppose that the first step of the polymer forming reaction would be the adsorption, through the lone electron pair, of a diazoethane molecule on the gold surface arising from the reduction of the gold halide used as primary catalyst:

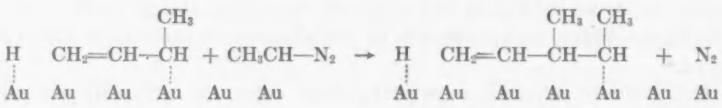


The polarization of the C—Au bond releases the N—C bond of the diazoalkane, nitrogen as a consequence is evolved, and highly unstable ethylidene fragments become bound to the metal surface. Part of these ethylidene fragments can be desorbed from the metal surface and rearrange to ethylene or react with a diazoethane molecule for giving an adsorption product which can be given off as butene-2 or initiate a polyalkylidene chain through a process of the Type:



leading to the formation of an initial vinyl-type unsaturation, has already been proposed as a working hypothesis.[2,3]

The growth of amorphous polyethylidene would be through the insertion of diazoethane from the solution at the end of the chain attached to the metal surface out of which the macromolecule grows:



This hypothesis would be supported by the fact that the apparent activation energy for the decomposition of diazoethane does not greatly differ from that for the process of amorphous polyethylidene formation.

The apparent activation energy of the process leading to crystalline polyethylidene is lower than that of formation of the amorphous product. It might be supposed that either the initiation or the termination steps of the crystalline polyethylidene chain are the same as for the amorphous one, and then the difference between the activation energies for the two processes would represent the difference between the activation energies for chain propagation. This difference might be explained by assuming that much probably crystalline polyethylidene would be formed through the addition at the end of the growing chain attached to the metal surface of diazoethane molecules adsorbed on neighboring sites.

If either diazoethane or the active end of the growing chains are strongly adsorbed, all the active centers of the gold surface would be occupied. As a consequence an apparent zero-order reaction for either diazoethane decomposition or polyethylidene formation would be observed, in agreement with what is experimentally found. Both the rates of diazoethane decomposition and of polyethylidene formation would then depend only upon the total number of sites at disposal, namely upon the total surface of the catalyst, and so an apparent first-order reaction against catalyst concentration, in agreement with the experimental results, is to be expected.

It has already been reported[3,4] that the infrared spectrum of either amorphous or crystalline polyethylidene shows some absorption bands which are peculiar to unsaturation of the vinyl type. A quantitative evaluation of these unsaturations, either by infrared spectroscopy or by chemical methods, lead to the conclusion that, as an average, there are two unsaturations per polymer molecule.

The molecular weight of amorphous polyethylidene increases with decreasing temperature of reaction as well as with decreasing concentrations of either the catalyst or diazoethane.[1,7] The observed dependence of the degree of polymerization of amorphous polyethylidene upon the initial concentration of diazoethane might suggest that chain transfer reactions with undecomposed diazoethane could be of some importance as chain termination processes. A transfer reaction of this type would, of course, lead to a second terminal unsaturation in the polyethylidene molecule, and this hypothesis would be supported by the fact that the number of unsaturation per polyethylidene chain is close to two.

The medium in which this kind of polymer forming reactions occurs plays a very important role. The different catalytic activity of copper surfaces towards polyethylidene formation when ethyl ether or aliphatic hydrocarbons are used as solvents and the fact that the presence of hydrogen during the reaction considerably increases polyethylidene yield when gold is used as a catalyst have already been reported.[2,4]

The results so far obtained concerning the influence of the solvent medium in the gold-catalyzed decomposition of diazoethene show that

either the processes of diazoethane decomposition or of crystalline polyethylidene formation are not so influenced by the solvent as the reaction of amorphous polyethylidene formation. This fact would support the hypothesis that the amorphous polymer would be formed through the addition to the active end of the growing chain of diazoethane molecules coming from the solution, while crystalline polyethylidene would arise from an interaction of the growing chain with adsorbed diazoethane molecules. A process of this type would depend upon the solvent only at a very little extent.

The influence of the solvent on the formation of the particles of colloidal gold from the reduction of the gold halide used as a primary catalyst is not, however, to be excluded, and this hypothesis might be taken to explain the small differences observed in the rates of crystalline polyethylidene formation passing from one solvent to the other.

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Synopsis

A suitable mechanism of reaction for the processes leading to amorphous and crystalline polyalkylidenes from the metal-catalyzed decomposition of diazoalkane solutions is proposed and discussed on the basis of the experimental evidences as obtained: (*a*) from the kinetic investigation of the formation of amorphous and crystalline polyethylidene from the gold catalyzed decomposition of ethyl ether solutions of diazoethane; (*b*) from the investigations on the degree of polymerization of polyethylidene, as related to diazoethane and catalyst concentrations; (*c*) from the data upon the temperature dependence of the rates of formation of both amorphous and crystalline polyethylidene; (*d*) from the temperature dependence of the degree of polymerization of polyethylidene; (*e*) from the results of the quantitative determination of the terminal double bonds on the vinyl type in the polyethylidene chain.

Résumé

Un mécanisme de réaction approprié aux réactions fournissant des polyalcoylidènes amorphes our cristallins par la décomposition de solutions de diazoalcane, catalysée par un métal, est proposé et discuté en rapport avec les résultats expérimentaux obtenus: (*a*) à partir de l'étude cinétique de la formation de polyéthylidène amorphe ou cristalline par décomposition de solutions de diazoéthane dans l'éther éthylique, catalysée par

l'or; (*b*) à partir de l'étude du degré de polymérisation du polyéthylidène en relation avec les concentrations en diazoéthane et en catalyseur; (*c*) à partir de l'influence de la température sur les vitesses de formation de polyéthylidène amorphe et cristallin; (*d*) à partir de l'étude de l'influence de la température sur le degré de polymérisation du polyéthylidène; (*e*) à partir des résultats obtenus lors de la détermination quantitative des doubles liaisons terminales du type vinylique dans la chaîne du polyéthylidène.

Zusammenfassung

Ein Reaktionsmechanismus für die bei der metallkatalysierten Zersetzung von Diazoalkanen in Lösung zu amorphen und kristallinen Polyalkylidenen führenden Prozesse wird vorgeschlagen und auf der Grundlage von Versuchsergebnissen bei (*a*) der kinetischen Untersuchung der Bildung von amorphem und kristallinem Polyäthyliden bei der gold-katalysierten Zersetzung von Äthylätherlösungen von Diazoäthan; (*b*) der Untersuchung der Abhängigkeit des Polymerisationsgrades von Polyäthyliden von Diazoäthan- und Katalysatorkonzentration; (*c*) der Bestimmung der Temperaturabhängigkeit der Bildungsbeschwindigkeit des amorphen und des kristallinen Polyäthylidens; (*d*) der Bestimmung der Temperaturabhängigkeit des Polymerisationsgrades von Polyäthyliden; (*e*) der quantitativen Bestimmung der endständigen Doppelbindungen vom Vinyltyp in der Polyäthylidenkette diskutiert.

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Directed Growth of Chains in Anionic-Coordination Polymerization

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The wide variation in polymer properties depends on the composition and structure of chains, which, in turn, are closely related to the nature of the initial monomers.

The basic factor determining the properties of polymers obtained by polymerization of the same monomers is the manner of polymer chain growth. The reactions involved differ in the type of active centers taking part in the chain propagation. These are free radicals, positive of negative ions, or catalytic complexes, which may be of very complicated structure.

Depending on the nature and structure of the active centers, the chain growth reactions result in monomer molecules entering a polymer chain in different ways; in various structures of chain links, and in a different order of their position within the chains. These reactions are characterized in some cases by high selectivity, i.e., by their ability to join molecules in a particular way.

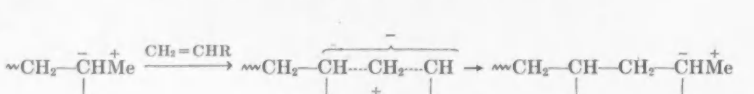
Thus, in studying polymerization there arises the important problem of making clear the natural laws of chain growth reactions, defining the structure of macromolecules being formed.

The available data show that ionic and particularly catalytic (coordination) polymerization processes present more possibilities of directing the chain growth than radical polymerization processes.

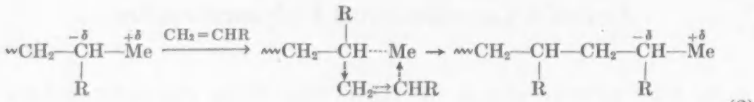
The present work considers some characteristics of such proceseses on the basis of examples of polymerization in the presence of alkali metals, as well as $TiCl_3$-AlR_3 type complex catalysts.

I. POLYMERIZATION INITIATED BY ALKALI METALS AND THEIR COMPOUNDS IN VARIOUS MEDIA

One of the principal problems in this field is the problem of the role of the metal and the medium in chain growth reactions. The reaction scheme [eqs. (1) and (2)] may serve as a basis for discussing the problem. The experimental basis is the results of earlier studies on polymerization processes initiated by alkali metals and their organic compounds.[1] This scheme, as a first approximation, may be represented by two extreme types of chain growth reactions. In the case of vinyl compounds it is as follows:



(1)



(2)

In the first type it is assumed that the charges in the terminal group are separated completely between the carbanion and the positive metal ion, a coulombic interaction alone acting between them (ionic bond). In this connection only one growing chain center and carbanion interact with a monomer in the transition state. The role of the metal is small in this case.

In the second type C—Me is a polarized covalent bond, and both the carbon and metal center participate in chain growth. [Reactions (1) and (2) do not present a detailed mechanism of real chain growth reactions, which includes such processes as active center association, solvation phenomena, and π-complex formation. The role of these processes will be discussed in the appropriate sections.]

In chain growth according to the second type one may expect the nature of the metal to affect greatly the direction of chain growth and the selectivity of the growth reaction to be very high because of double-center interaction. This chain growth reaction type will be designated as a coordination type, and the former as an anionic type.

Real polymerization processes initiated by alkali metals and their compounds are represented by the two growth reaction types; the majority of the processes are of an intermediate type, and thus these processes are called anionic-coordination polymerization.

The relationship between the two chain growth types for the same monomer or a mixture of monomers is determined by the nature of the metal and the medium.

The magnitude of the polarity of C—Me bond is dependent approximately on the ionization potential, which is the most important characteristic of the metal. Consequently the C—Me bond polarity, and therefore anionic form of growth must increase in the following sequence:

$$\underset{5.37}{\text{Li}} < \underset{5.09}{\text{Na}} < \underset{4.32\ \text{e.v.}}{\text{K}} \qquad \text{(series A)}$$

The coordination form of growth increases apparently in reverse direction. The other important characteristics of a metal, together with the properties of the medium affecting the initial C—Me bond polarity, are valence electron level and metal ion radius, which determine the electron-accepting properties. The lower the free valent levels are and the less the metal ion radius, the stronger the solvation and complex formation of the metal with electron-donating compounds.

Solvation and complexing increase C—Me bond polarity. These properties of alkali metals increase in the following order, which is reverse to that of series A:

$$K < Na < Li \qquad \text{(Series B)}$$
$$1.33 \quad 0.95 \quad 0.6 \text{ (ion radius, A.)}$$

The significance of this factor is very high and in some cases it may result in the transformation of the principal chain growth type. Polymerization in the presence of lithium alkyls in a hydrocarbon medium for instance, proceeds by a coordination reaction of the type (2).

Anionic type (1) prevails in solvents with strong electron-donating groups (e.g., tetrahydrofuran), a complex ion $Li^+ \cdots O<$ being cation:

$$\sim\!\sim CH_2\!-\!\overset{\overset{-\delta}{|}}{\underset{\underset{R}{|}}{CH}}\!-\!\overset{\overset{+\delta}{|}}{Li} + :O< \;\rightarrow\; \sim\!\sim CH_2\!-\!\overset{\overset{-}{|}}{\underset{\underset{R}{|}}{CH}}\;\; \overset{+}{Li}\cdots O<$$

This effect also explains the well known fact, that the anionic type becomes the prevailing one in strongly electron-donating media irrespective of the kind of alkali metal.

It should be pointed out that the monomer molecule can be the solvating agent too, since the double bond can be the source of electrons as is known from the formation of π-complexes with Lewis acids.

As a conclusion it must be noted that the anionic form of growth increases, without any solvation phenomena, in the succession A. The solvation effect results in anionic form growth according to succession B. Therefore the relationship between the two types of chain growth depending on metal and medium is determined by the result of the two competing factors.

With regard to this scheme we will consider the investigation results obtained in the study of the effect of Li, Na, and K on polymer chain growth in butadiene polymerization initiated by these metals and their compounds in various solvents.

This work has been carried out in our laboratory by R. V. Basova, A. A. Arest-Yakubovich, D. A. Solovikh, and N. V. Desiatova.

Experimental Conditions

The purification of monomers and solvents and the experimental procedure have been described in previous reports.[2-6] The charging of the reagents and the polymerization were carried out at high vacuum. The polybutadiene structure was determined by an infrared method, characterized by frequencies 909 (1,2), 730 (1,4-*cis*) and 967 (1,4-*trans*) cm.$^{-1}$.

Lithium ethyl (LiR), sodium metal, sodium naphthalene (SN), potassium metal, potassium naphthalene (PN), and organopotassium compounds (OPC) were used as initiators. The organic potassium compounds were obtained by isoprene polymerization initiated by potassium metal (mirror) in toluene. These are a mixture of potassium benzyl and isomerized

carbanion of polyisoprene of low molecular weight (K ≅ 22 wt.-%), precipitating in polymerization. These are very convenient and pure initiators, soluble completely under polymerization conditions. Benzene, toluene, heptane, cumene, tetrahydrofuran (THF), and triethylamine (TEA) were solvents and additives.

The content of 1,2-structures in polybutadiene may be chosen as the principal parameter defining the effect of metal and medium on chain growth. In the anionic chain growth type it is this structure that is mainly formed (up to 95%). It is obvious that the reduction of the amount of 1,2-structure formed indicates an increase of coordinating effect of metal in the chain growth.

The main results of the studies are given in Table I.

TABLE I
Effect of Polymerization Conditions on Polybutadiene Structure

No.	Initiator	Medium	Additive	Additive, vol.-%	Temperature of polymerization, °C.	Polybutadiene structure, %		
						1,2	1,4-*cis*	1,4-*trans*
1	Lithium ethyl	Heptane[a]	—	—	30	6.8	42.8	50.4
2	" "	Toluene[a]	—	—	30	8.7	43.7	47.6
3	Na	Benzene	—	—	25	32.3	22.6	45.0
4	Na	Toluene[b]	—	—	25	31.5[c]	23.7	44.8
5	K	Benzene	—	—	25	35	16.5	48.5
6	K	Benzene–heptane (5:1)	—	—	0	38.1	12.8	49
7	OPC	"	—	—	0	45	12	43
8	Radical polymerization[8]	Hydrocarbon	—	—	5	18	10	72
9	Lithium ethyl	Benzene	TEA	10	25	37.1	22.8	40
10	Na	"	"	10	25	43.3	17.3	39.4
11	K	"	"	10	25	37.4	16.6	46.0
12	Lithium ethyl	"	THF	1	25	73.6	13.3	13.1
13	Na	"	"	1	25	44.3	12.8	42.8
14	Lithium ethyl	Heptane	"	6	−50	91.5	4.1	4.4
15	SN	Cumene	"	6	−50	88	—	12
16	PN	Heptane	"	6	−50	61.6	5.1	33.3
17	OPC	Cumene	"	6	−50	58.8	5.8	35.4
18	PN	"	"	15.5	−50	61.7	5	33.3
19	SN	THF	—	—	−50	88	—	12
20	SN	"	—	—	−90	92.8	—	7.2
21	PN	"	—	—	−50	84.7	—	15.3
22	Lithium ethyl	"	—	—	−50	91	—	9

[a] Polymers obtained in previous study.[5]

[b] When butadiene was polymerized in toluene with sodium and potassium the molecular weight of polybutadiene was much lower than that in benzene or heptane, as a result of chain transfer reactions.

[c] The possibility to produce polybutadiene with low content of 1,2-structures was reported previously.[7]

From the data given in the table it is evident, that the kind of alkali metal affects polymer structure most greatly in hydrocarbon solvents (see Nos. 1, 2, 3, 4, and 5).

If there is no solvation, the degree of participation of metal in chain growth reactions should increase with the increase of alkali metal ionization potential which actually takes place.

The values for the 1,2-structure fraction in the experiments with metals are smaller than those expected, as a result of radical participation in the process.

Corresponding data for radical polymerization are given in experiment 8. The effect of the processes on polybutadiene structure is evident from the comparison of experiments 6 and 7, in which radical polymerization is excluded.

The relatively small difference in 1,2-structures formed with Na and K (expts. 3, 4, and 5) may be related to their different degree of solvation with monomer. However this effect is insignificant. As was pointed out, sodium is solvated to a higher degree than potassium in accordance with sequence B.

A considerable effect of solvation phenomena on chain growth reactions may be confirmed by the comparison of the results obtained from the experiments with Li, Na, and K in hydrocarbon solutions (expts. 1–5) to those from the experiments carried out under the same conditions but with 10% TEA added expts. 9–11. As is shown in the previous studies,[1,2] TEA is a relatively weak electron donor.

As one can see from the data of Table II, the 1,2-structure fraction increases rapidly with the addition of TEA in the case of lithium, the increase being much less in the case of sodium and very small in the case of potassium.

TABLE II

	1,2 Structure, %	
Metal	Hydrocarbon	Hydrocarbon + 10% TEA
Li	8.7	37.1
Na	31.5	43.3
K	35.0	37.1

Thus the participation of metals in chain growth in nonpolar media corresponds to the reverse succession A predicted in polymerization with lithium, sodium, potassium, and their organo-compounds in hydrocarbon solutions. In polar media the solvation effects are of great importance, and are stronger in the case of sodium than with potassium.

In connection with our results it should be noted that the unexpected dependence between coordinating capacity of alkali metal and its nature (Na < K), found by other authors in hydrocarbon media in polymerization

TABLE III
Effect of Alkali Metal and Medium on Butadiene Polymerization Rate

No.	Initiator	Initiator concentration, mmole/l.	Initial monomer concentration, mole/l.	Solvent	Additive	Additive, vol.-%	Temperature, °C.	v, l./mole-sec.[a]	Amount 1,2 structure, %
1	Li Ethyl	1.65	2.8	Heptane	THF	6.0	−50	0.003	91.5
2	SN	2	2.5	Heptane	THF	6.5	−50	0.006	88.0
3	PN	2.3	3.1	Heptane	THF	6.0	−50	0.005	84.7
4	Li Ethyl	5	1.0	Toluene	—	—	0	0.0006[b]	8.7
5	OPC[c]	1	1.35	Benzene-heptane (5:1)	—	—	0	0.09	45.0
6	OPC[c]	1.5	1.65	Toluene	—	—	0	0.08	

[a] The rate of chain growth, referred to concentrations of monomer and catalyst. If there is no association of growing chains, $V = K_p$ (propagation rate constant).

[b] The value is calculated from previously reported data.[5]

[c] When initiated by OPC, polymerization was carried out in a dilatometer with an agitator. After short induction period the polymerization proceeded at stationary conditions.

of conjugated diene monomers[9–12] was apparently due to traces of solvating admixtures, which interact to a greater extent with sodium than with potassium.

When electron-donating solvents are introduced into hydrocarbon medium, the solvation (or complexing) factor acquires an importance, which increases the role of anionic mechanism in chain growth and, consequently, the 1,2-structure fraction in the polymer. Thus the addition of a strong electron donor (THF) to hydrocarbon medium to the extent of 1% causes considerable change in the structure of polybutadiene obtained by polymerization initiates by organo-sodium and especially organo-lithium compounds (see expts. 3, 2, 13, and 12). With 6% THF the structure of polybutadiene, obtained with these initiators differs little from the structure obtained in pure (100%) THF (see expts. 15, 14, 19, 22).

In the polymerization initiated by potassium or organo-potassium compounds, the addition of both THF and TEA, as one should expect, alter the polybutadiene structure to a much lesser degree. Even with 15% THF the content of 1,2-structures is considerably lower, than that with 100% THF.

It should be noted that in the presence of electron-donating solvents the ratio of anionic and coordination forms depends on temperature. The comparison of experiment 19 and 20 shows the 1,2-structure fraction in polybutadiene rises with decreasing reaction temperature, which is due to higher activation energy of chain growth reaction of the coordination type, than that of the anionic type.

It is interesting in this connection that the polymerization rate and the formation of 1,2-structures in polymer are not always in the same correlation. Our data on the kinetics of butadiene polymerization initiated by organic compounds of lithium, sodium, and potassium in hydrocarbons with small quantities of THF are presented in Table III. According to these results, the lowest reaction rate was observed in the case of organolithium compounds, despite the fact that the highest amount of 1,2-structure fraction was obtained (see table III, expts. 1–3).

A still sharper decrease of the reaction rate, when organolithium initiators are used instead of organopotassium compounds takes place in hydrocarbon medium (expts. 4–6). Such a sharp difference in the rates is due not only to the change of the reaction type, but is probably also the result of increasing active center association in the case of lithium as compared to that of potassium. It is clear that the increased association results in a reduced number of effective polymerization centers.

Copolymerization

The data on composition of copolymers produced by copolymerization of isoprene and butadiene with styrene initiated by organolithium, sodium, and potassium compounds, are given in Table IV. These data show that in this case the main features of anionic-coordination polymerization also become apparent.

TABLE IV
Composition of Copolymers Obtained in Presence of Different Alkali Metals and their Compounds in Different Media at an Initial-Mol Ratio of Monomers

No.	System	Initiator	Medium	Temperature, °C.	Styrene in copolymer, %	Reference
1	Isoprene–styrene	Li Ethyl	Toluene	27	12	2
2	"	Na	"	25	56	13
3	"	K	"	0	70	6
4	"	OPC	"	0	75	6
5	"	Li Ethyl	THF	27	82	1,2
6	"	Li Ethyl	THF	−35	97	1,2
7	Butadiene–styrene	Li Ethyl	Toluene	25	9	1,2
8	"	Na	Hydrocarbon		50	7
9	"	OPC	Toluene	0	67,5	6
10	"	Li Ethyl	THF	−35	85	1,2

As appears from the given values the anionic type reactions of chain growth in these processes are characteristic of the enrichment of the resulting product by styrene (isoprene < butadiene < styrene).

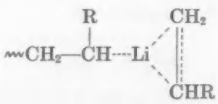
The anionic form should increase in hydrocarbon media according to sequence A: Li < Na < K, i.e., participation of metal in chain growth increases in reversed order. As is shown from considering isoprene–styrene and butadiene–styrene copolymerization, this indeed takes place.

Here also, as it was mentioned above, with potassium the radical reactions participate in chain growth to a certain (small) extent (see expts. 3 and 4).

When polymerization is carried out in electron-donating media (THF) the role of the anionic component rises in accordance with electron-accepting properties of the corresponding metal.

The lower the temperature, the greater the role of the anionic type reactions (see expts. 5 and 6).

However, considering the composition of copolymer formed in hydrocarbon media, the properties of the two-stage chain growth should be taken into account. The possibility of such a mechanism was pointed out in earlier studies on polymerization initiated by lithium alkyls.[1–5] The characteristic feature of the mechanism is the formation of a metal–monomer π-complex of the type



previous to the transition state.

The rearrangement of the complex at the transition state results in an act of chain growth. Therefore, copolymer composition is determined as a result of two reactions: (*1*) formation of π-complex with a monomer mole-

cule and (2) its entry into a polymer chain. Two monomers participating in polymerization may differ much by their extent of participation in the above two reactions.

Chain Transfer Reactions in Polymerization with Organometallic Compounds

The anionic-coordination character of the reaction also becomes apparent in the case of chain transfer in polymerization initiated by alkali metals or their organic compounds:

$$\sim\!\!\sim CH_2\!-\!\underset{\displaystyle R}{\underset{|}{CH}}\!-\!Me + HR' \rightarrow \sim\!\!\sim CH_2\!-\!\underset{\displaystyle R}{\underset{|}{CH}} + R'Me$$

The probability of chain transfer reactions may be expected to increase with increasing C—Me bond polarity, when the same hydrocarbon solvent HR and monomer are used, i.e., the probability increases in the order Li < Na < K. In other words, with an increase in the role of the anionic form in chain transfer reactions the molecular weight of the resulting polymer decreases. In fact, it was shown, that the polymerization of butadiene, isoprene, and styrene[2,14,15] in benzene or toluene solutions proceeds by the mechanism of "living" chains, and molecular weights are determined by the ratio $\Delta M/C_{cat}$. Chain transfer does not take place in these cases.

A different situation was observed in the polymerization of styrene, isoprene, and butadiene initiated by potassium and sodium metal and their compounds. These investigations were carried out in our laboratory by R. V. Basova. Polymerization was performed under vacuum in a cylindrical glass vessel, the internal surface of which was coated with a fine film of potassium metal. The detailed data and procedure were described in a previous report;[6] some of them are given in Table V (see expts. 1–5 and 8–12).

Even from these qualitative results the dependence of molecular weight on nature of hydrocarbon solvent can be seen. The dependence appears to be especially sharp in comparing benzene with toluene due to an elevated proton-donating capacity of the latter.

The most precise data on molecular weight variation dependence on solvent were obtained in butadiene polymerization in the presence of organopotassium compounds (Table V, expts. 13 and 14), prepared by the procedure mentioned earlier, and potassium naphthalene (see table V, expts. 15 and 16).

Investigation of the C—Me Bond by Absorption Electron Spectra

At present there have been published a considerable number of studies making use of electron spectra as a method for investigation of the C—Me bond (where Me is an alkali metal).[15,19–23] However, the results of these investigations still are insufficient to evaluate the efficacy of the method in solving the problem.

TABLE V
Molecular Weights of Polydienes Obtained Under Various Conditions

No.	Monomer	Initiator	Initiator concentration, mole/l.	Solvent	Additive	Additive, vol.-%	Monomer concentration, mole/l.	Temperature, °C.	Molecular weight[a]
1	Styrene	K		Benzene			2.7	25	350,000
2	Styrene	K		Toluene			2.7	"	135,000
3	Isoprene	"		Benzene			2.0	"	168,000
4	Isoprene	"		Toluene			2.0	"	7,400[c]
5	Isoprene	"		Cumene			2.0	—	126,000
6	Butadiene	Li Ethyl	5×10^{-5}	Heptane			1.6	30	1,960,000
7	"	Li Ethyl	2.2×10^{-3}	Toluene			1.6	30	4,250,000
8	"	Na[b]		Benzene			2.4	25	450,000
9	"	Na[b]		Toluene			2.4	"	13,000
10	"	K		Benzene			2.4	"	362,000
11	"	K		Toluene			2.4	"	41,700
12	"	K		Cumene			2.7	"	364,000
13	"	OPC[d]	1×10^{-3}	Benzene–heptane (5:1)			1.35	0	40,000
14	"	OPC[c,d]	1.47×10^{-3}	Toluene			1.65	0	4,000
15	"	PN[d]	2×10^{-3}	Heptane	THF	4	1.1	−25	35,600
16	"	PN[c,d]	2×10^{-3}	Toluene	THF	4	1.1	−25	8,000

[a] Unless otherwise indicated, molecular weights were determined by a viscometric method and calculated by the following equations: (1) polystyrene:[16] $[\eta] = 1.55 \times 10^{-4} M^{0.74}$; (2) polyisoprene:[17] $[\eta] = 5.02 \times 10^{-4} M^{0.667}$; (3) polybutadiene:[18] $[\eta] = 2.7 \times 10^{-4} M^{0.725}$.

[b] Data obtained by D. A. Solovykh.

[c] Molecular weights were determined by an ebullioscopic method.

[d] Conversion = 60%.

Difficulties encountered in using this method are due to high sensitivity of the systems under study with regard to traces of various admixtures. Moreover, these systems are unstable in some cases owing to side reactions. For instance, Szwarc et al.[23] have shown that sodium polystyrene and sodium benzyl isomerize both in THF and hydrocarbons to form more stable compounds which are characterized by an absorption band of greater wavelength. The rate of the processes increases with the increase of temperature and medium polarity.

The electron spectra of "living" unisomerized polystyrene were found to change little when an exchange of Li for Na or K was made and when hydrocarbon media were used instead of those which are electron-donating.[15]

Similar results have been obtained by us in studying spectra of some polydienes (see Table VI).

In order to evaluate more carefully the possibilities of the method for studying the C—Me bond D. K. Polyakov and Yu. L. Spirin in our laboratory have determined the electron absorption spectra of a number of polymers, copolymers of various monomers (dienes, styrene, 1,1-diphenylmethane, anthracene), and derivatives of some other compounds (triphenylethylene, triphenylchloromethane, fluorene).

The work was carried out by means of completely sealed quartz cell in a CF-4 spectrophotometer; the materials were of high purity. Most monomers and solvents had been treated with lithium ethyl and then recondensed

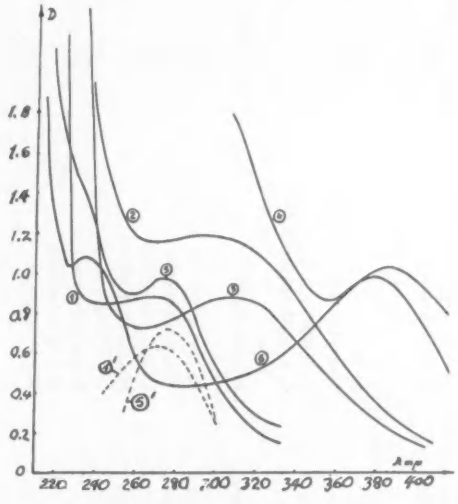
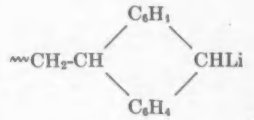


Fig. 1. Electron spectra of polydiene carbanions: (*1*) lithium polyisoprene in hexane; (*1'*) the same without "dead" polymer; (*2*) lithium polybutadiene in THF; (*3*) sodium polyisoprene in hexane; (*4*) sodium polybutadiene in THF; (*5*) sodium polybutadiene in THF (low conc. NaR); (*5'*) same without "dead" polymer; (*6*) potassium polyisoprene in THF.

TABLE VI

Absorption Spectra of Carbanions at Various Conditions (Temperature 25°C.)

No.	Medium	Me—R	λ_{max} of carbanions, mμ	λ_{max} of isomerized carbanions, mμ	Note
1	Benzene	Li-polystyrene	333	430–460 530–560 Very weak	Band of isomerized carbanion visible at high concentration of the compound in the solution.
2	THF	Li-benzyl	330	375	λ_{max} = 375 after three days.
3	Benzene	Li-α-Methylstyrene carbanion	338		Obtained by reaction of α-methylstyrene with Li ethyl
4	THF	K-α-methylstyrene carbanion	338		
5	Benzene	Na-polystyrene	335–340	400–450 520–550	In the course of time the intensity of the band at 335–340 mμ decreases, that of other bands increases.
6	Hexane	Li-polyisoprene	276		
7	Hexane	Na-polyisoprene	—	306	Band is large and covers a wide range of wavelengths.
8	Hexane	Li-polybutadiene	276		
9	Hexane	Na-polybutadiene		300–320	"
10	THF	Li-polybutadiene Li-polyisoprene	280	310	Diffused maximum
11	THF	K-polybutadiene	–	235; 375[a]	Bands at 235 and 375 mμ appear in polymerization.
12	THF	K-polyisoprene	280 (weak)		After addition of isoprene to the product of expt. 11
13	Hexane	$C_3H_7(C_6H_5)_2CLi$	410		
14	Benzene	"	420		
15	Amine	"	435		
16	THF	"	490		
17	Toluene	$\sim\sim CH_2(C_6H_5)_2C—Na$	455		Obtained by the addition of 1,1-diphenylethylene to Na-polybutadiene

18	Benzene			420	Obtained by the addition of anthracene to lithium polystyrene
19	Benzene	"	Na	445	Obtained by the addition of anthracene to sodium polybutadiene
20	THF	"	Na	445	Obtained by the addition of anthracene to sodium polystyrene
21	Amine	$(C_6H_5)_3CLi$		440	
22	THF + amine	"		440 (weak) 500 (intense)	
23	Benzene	$(C_6H_5)_3CNa$		472	
24	THF	"		490	
25	Benzene	$(C_6H_5)_2CK$		490–500	
26	Benzene	Lithium florenyl		450 (intense) 480–530	
27	THF + benzene	Lithium fluorenyl		454, 487 (intense) 520, 554 (less intense)	
28	Benzene	Same as expt. 27, but after prolonged vacuum pumping		415, 440 (less intense) 470 (intense)	

[a] Band λ_{max} = 375 was also observed in previous work,[20] where it was supposed to be due to unisomerized allyl carbanion.

into the cell. All the procedures had been carried out under vacuum. The results obtained are given in Table VI and Figures 1 and 2.

As it is evident from the figures, the spectra of the investigated compounds are characterized by small number of well resolved bands.

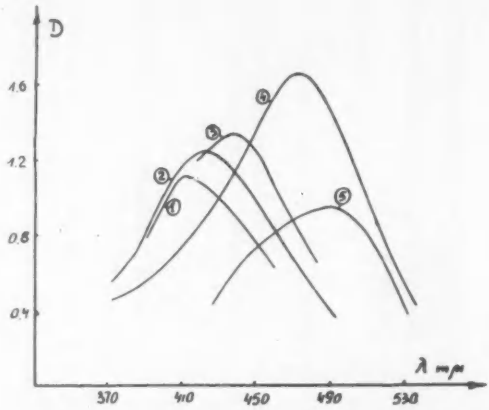


Fig. 2. Absorption electron spectra of 1,1-diphenylalkyl carbanions: (*1*) 1,1-diphenylethene + LiEt in hexane; (*2*) 1,1-diphenylethene + LiEt in benzene; (*3*) 1,1-diphenylethene + LiEt in TEA; (*4*) 1,1-diphenylethene + Na in THF; (*5*) 1,1-diphenylethene + LiEt in THF.

As follows from the data in Table VI (expts. 1–5, 8, 10–12), the electron spectra of unisomerized "living" polymers of isoprene, styrene, and butadiene practically do not depend on the metal (Li, Na, K) and electron-donating capacity of the solvent used. However, an appreciable shift of absorption bands and a change of their intensity have been found in studying the spectra of corresponding compounds of triphenylmethane, 1,1-diphenylethylene, fluorene, and anthracene, depending on alkali metal and medium used (Table VI, expts. 13–28). The sharpest effects were observed with lithium, sodium, and potassium compounds of triphenylmethyl and diphenylalkyl. A smaller effect of metal and medium on spectra had been discovered for anthracene and fluorene compounds, the phenyl rings of which are fixed in their positions with five- or six-membered rings.

The identity of electron spectra of polystyrene and polydiene compounds with various alkali metals appears to be the result of structural peculiarities inherent to these systems.

If there is only one substituent (vinyl or phenyl group) on the C-atom of the C—Me bond, this carbon atom is always in the plane of the substituent.

If these are two or three phenyl groups on the carbon atom, the change of C—Me bond polarity results in the change of the spacial arrangement of these substituents. This changes the λ_{max} of the corresponding absorption band.

The electron spectra of the investigated compounds can also be affected to some extent by the degree of their association. For instance, the large effect observed in the case of polynuclear compounds can be explained to some extent by steric hindrance to the association of such molecules.

In considering hydrocarbon monomer polymerization initiated by various alkali metals or their organic compounds in nonpolar media, a number of suppositions were made as to the nature of active centers. One of them is based on different C—Me bond polarities[1,11] and another one treats the discovered relations as resulting from different properties of the counterion in the $\overset{-}{\text{L}}\overset{+}{\text{M}}$E ion pair.[14,15] Besides, a supposition was stated, that the active centers represent an equilibrium mixture of both kinds.[24] It is unlikely that these problems can be solved finally at present.

However, the available information on the dependence of electron absorption spectra on the nature of alkali metal and medium do credit to the concept of different C—Me bond polarity in hydrocarbons, and point to the small probability of its dissociation under these conditions. The above relations valid for chain transfer reactions in the presence of various metals and solvents confirm this conclusion to some extent.

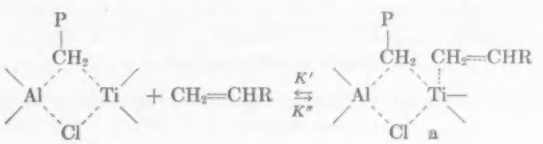
II. POLYMERIZATION INITIATED BY α-$TiCl_3$–AlR_3 SYSTEM IN HYDROCARBON SOLVENTS

The study of these processes were carried out in our laboratory by E. V. Zabolotskaya, L. M. Lanovskaya, and V. A. Khodzhemirov.

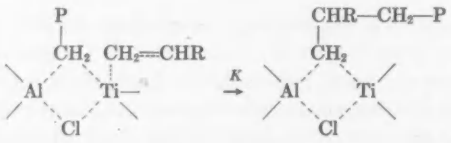
It was pointed out earlier, that the complex catalytic system presents the greatest possibilities for the control of chain growth reactions and their selectivity.

In the present paper are reported some peculiarities of these reactions noted in a study of ethylene polymerization in the presence of various monomers, and the homo- and copolymerization of styrene and isoprene in the presence of systems of the type AlR_3–α $TiCl_3$ in hydrocarbons. These processes, according to the terminology adopted by us, belong to the coordination type. There are insufficient experimental data to permit consideration of the polar mechanism.

The main peculiarity of these catalytic systems for chain growth reactions in the presence of P—Ti bonds (where P denotes the polymer chain). According to the concept developed by a number of investigators, this bond is a part of the catalytic bridge complex.[25–27] Chain growth reactions proceed in accordance with eqs. (3) and (4):



(3)



(4)

This complex may be presented in first approximation as a double-centered system, in which the first sorption center (a) fixes the monomer molecule and the second reaction center connects the adsorbed monomer molecule to the "root" of the growing chain. The complex compound formation of the titanium catalyst component and monomer molecule is the essential stage of the above reactions. The existence of this stage has been confirmed by experiments carried out to determine the inhibiting effect of various monomers (which are not polymerized under the experimental conditions) in ethylene polymerization.

Small quantities of isoprene and butadiene were found to decrease the ethylene polymerization rate in the presence of α-$TiCl_3$–AlR_3 at 25°C.[3,27]

The formation of complex compound is determined by the interaction of monomers with the Ti component. According to the data on copolymerization of ethylene and propylene, the copolymer composition of this system depends appreciably on the metal of the transition group[28] and little on the nature of metal in the metal alkyl[29] catalyst component. The structure of the resulting complex compound is determined by the peculiarities of the titanium atom, which was both electron-accepting and electron-donating properties (in contrast to atoms of Li and Al in the compounds LiR and AlR_3, which are characterized by electron-accepting properties only).

More detailed information on chain growth reactions was obtained in a study of homo- and copolymerization of styrene and isoprene.

Considering the chain growth reactions in copolymerization of these monomers, some peculiarities must be taken into account, which are revealed both in the adsorption (the formation of a complex with the Ti component) and in the reaction processes.

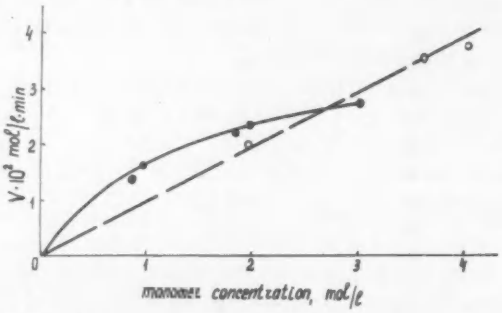


Fig. 3. Dependence of the rate of homopolymerization of styrene and isoprene on monomer concentration (t = 75°C.).

The experiments carried out to show the dependence of homopolymerization rate on monomer concentrations (Fig. 3) indicate that the rate of styrene polymerization is proportional to styrene concentration throughout the investigated concentration range.[30] This indicates a very small value for the adsorption process (complexing of monomer with titanium catalyst component). In the case of isoprene this dependence is characterized by a saturation curve, which indicates a large adsorption value, limiting the rate of its polymerization.

In view of the above considerations the rate of styrene (A) and isoprene (B) entering a polymer chain in copolymerization is determined by eqs. (5) and (6):

$$-dA/dt = K_A{}^*{}_A\sigma_A p_A(1 - \sigma_B) + K_B{}^*{}_A\sigma_A p_B(1 - \sigma_B) \tag{5}$$

$$-dB/dt = K_B{}^*{}_B\sigma_B p_B + K_A{}^*{}_B\sigma_B p_A \tag{6}$$

where σ_A and σ_B are the fraction of titanium centers joined to styrene and isoprene molecules, respectively, in homopolymerization; K_{A*A} and K_{B*B} are the rate constants of chain growth in homopolymerization of styrene and isoprene, respectively; $K_A{}^*{}_B$ and $K_B{}^*{}_A$ are the rate constants of reactions of adsorbed isoprene and styrene molecules, respectively, with roots of growing chains of types A* and B*; and P_A and P_B are the fractions of terminal styrene and isoprene links (roots) of growing chains A* and B*.

The solution of these equations leads to eq. (7) for the differential copolymer composition:

$$\frac{dA}{dB} = \frac{[A]}{[B]} \frac{\dfrac{K_A{}^*{}_A \cdot K_A}{K_A{}^*{}_B \cdot K_B} + 1}{\dfrac{K_B{}^*{}_B \cdot K_B}{K_B{}^*{}_A \cdot K_A} + \dfrac{[A]}{[B]}} = \frac{[A]}{[B]} \frac{r_A[A] + [B]}{r_B[B] + [A]} \tag{7}$$

This equation differs from the usual one by the reactivity of ratios, which include adsorption constants for the two monomers:

$$K_A = K_A'/(K_A'' + K_A{}^*{}_A)$$

and

$$K_B = K_B'/(K_B'' + K_B{}^*{}_B)$$

where K_A', K_A'' and K_B', K_B'' are adsorption and desorption constants for styrene and isoprene, respectively.

The values for some constants calculated from the data on homo- and copolymerization of styrene and isoprene are given in Table VII. The constants of reactions taking place on the $TiCl_3$ surface are referred to the surface of one mole $TiCl_3$ with a particular and uniform grain size.

It follows from the given values of r_A and r_B determining copolymer composition that the copolymers should be enriched with isoprene, which actually takes place (see Fig. 4).

TABLE VII
Constants of Homo- and Copolymerization

Constants of homopolymerization	Dimension	Reactivity ratios
$K_{A^*A}K_A = 1 \times 10^{-2}$	l./mole min.	$r_A = \frac{K_{A^*A} \cdot K_A}{K_{A^*B} \cdot K_B} = 0.1$
$K_{B^*B} = 4.15 \times 10^{-3}$	$min.^{-1}$	$r_B = \frac{K_{B^*B} \cdot K_B}{K_{B^*A} \cdot K_A} = 6.0$
$K_B = 0.65$	l./mole	$r_1 = \frac{K_{A^*A}}{K_{B^*A}} = 2.2$
$K_{B^*B}K_B = 2.7 \times 10^{-2}$	l./mole min.	$r_2 = \frac{K_{B^*B}}{K_{A^*B}} = 0.27$

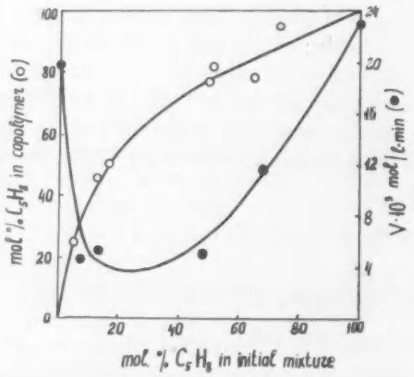


Fig. 4. Dependence of (●) copolymerization rate and (○) copolymer composition in the system isoprene–styrene on the initial monomer mixture ($t = 75°C.$); total monomer concentration = 2 mole/l.

On the other hand, the comparison of values $r_1 = K_{A^*A}/K_{B^*A}$ with $r_2 = K_{B^*B}/K_{A^*B}$ (Table VIII) calculated on the basis of the constants for homo- and copolymerization[31] points to higher reactivity of the styrene "root" center A^x than that of the isoprene center B*.

The effective monomer concentration on the catalyst surface is determined by the adsorption ratio $K_A[A]/K_B[B]$, where $K_A \ll K_B$. In the addition of a small quantity of isoprene to styrene $K_B[B] > K_A[A]$. This leads to the preferential polymerization of isoprene; the fraction of the reaction centers P_A of high reactivity is reduced considerably at the expense of centers P_B having lower reactivity. Therefore, the introduction of small quantities of isoprene into styrene causes a sharp decrease of copolymerization rate (Fig. 4).

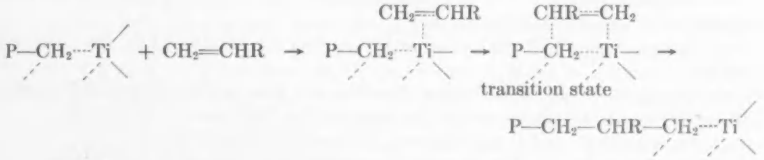
TABLE VIII
Activation Energy in Polymerization of Ethylene and Propylene in the Presence of Various Metal-Alkyls

No.	Monomer	Metal-alkyl	E, kcal./mole[a]
1	Ethylene	$AlEt_3$	7.6
2	"	$Al\text{-}Bu_3$	8.3
3	"	$AlEt_2Cl$	7.8
4	"	$ZnEt_2$	8.0
5	Propylene [34,35]	$AlEt_3$	13.6
6	"	$Al\text{-}Bu_3$	14.2
7	"	$BeEt_2$	16.2

[a] E values were calculated taking into consideration the change of monomer concentration with temperature.

Further, the curve showing the relation of the composition of initial reagents on the rate goes through a minimum, and with a considerable increase of isoprene concentration the rate increases, too.

Thus the chain propagation reactions can be presented by the following scheme:



This scheme is similar to that of chain growth in the polymerization with organo-lithium compounds in hydrocarbons, with the difference that the catalyst acts in the form of a bridged complex. In this connection there arises a question on the role of the aluminum component in chain growth reactions.

A number of investigators believe the role of metal alkyls consists in the alkylation and reduction of the titanium component, as well as chain transfer.[29,32,33]

As the basis of the latter scheme the data of Carrick[29] were taken, according to which the nature of the metal in the metal-alkyl component does not affect the composition of copolymers of ethylene with propylene. Our results of investigation of the effect of the metal-alkyl component on ethylene polymerization kinetics in the presence of α-$TiCl_3$, as well as the data on propylene polymerization kinetics obtained earlier[34,35] show that the metal in metal-alkyl component has very little effect on activation energy of the polymerization process (see Table VIII). This points to the determining role of the Ti—P bond in chain growth reactions, which was the basis for the present treatment.

However, it should be noted, that alkyl compounds of transition metals in their lower state valence are not stable. Natta et al.[36] have shown in

their x-ray investigations of soluble compounds of titanium with AlR_3 that the formation of complex compound of the above mentioned structure does indeed take place.

These considerations suggest that the metal-alkyl component of catalyst not only reduces and alkylates compounds of transition metals, but also stabilizes these compounds by the formation of bridged bonds.

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Synopsis

Results obtained in the investigation of the polymerization of conjugated dienes, catalyzed by organic lithium, sodium, and potassium compounds, show that in hydrocarbon media, these processes take place by an anionic-coordination mechanism, whose essential characteristic is the participation of two centers in the chain growth reaction: these centers are the metallic and hydrocarbon components of the growing chain. The degree of participation of the alkali metal in the growth process decrease in the order: Li > Na > K. Lithium compounds participate strongly, in conformity with the coordination character of the chain growth reaction. The use of sodium and potassium results to a significant extent in an anionic type of chain growth reaction. On introduction of electron-donor compounds in the hydrocarbon medium, the anionic type reaction becomes the predominant one in all cases. The hypothesis of the anionic-coordination mechanism of polymerization in the presence of organoalkali metal compounds is confirmed not only by the results of the investigation of the structure of the formed polydienes, but also by the data of copolymerization, by the results of a study of the reaction of chain transfer with these catalysts, and even by the results obtained by a spectrophotometric investigation of the corresponding organometallic compounds. The catalyst AlR_3-$TiCl_3$ is another example exhibiting the specific characteristics of the two-center catalytic polymerization system, which selectively controls the chain growth reaction. Investigation carried out with the help of this system, in the polymerization of ethylene in the presence of different monomers, in the homopolymerization and copolymerization of styrene and isoprene show that the catalyst is an electron-deficient four-membered system, which, as a first approximation is characterized by the presence of two centers: an absorption center which forms a complex with monomers, and a reactive center (the "root" of the growing chain) which joins the absorbed molecule of monomer to the growing chain. A detailed examination of the copolymerization of styrene and isoprene show, that sequence of monomer union in the polymer chain is determined by the combination of the two acts, the reaction rate of which is dependent on the nature of the monomer and the "root" of the growing chain.

Résumé

Les résultats observés dans les recherches sur les polymérisations des dienes conjugués, initiées par des composés organolithiques, sodiques et potassiques montrent qu'en milieu hydrocarboné, ceux-ci ont lieu par un mécanisme de coordination anionique qui est essentiellement caractérisé par une participation de deux centres dans la réaction de croissance de chaîne: ces centres sont les composés métalliques hydrocarbonés de la chaîne en croissance. Le degré de participation du métal alcalin dans le processus de croissance diminue dans l'ordre suivant: Li > Na > K. Les composés lithiés présentent une forte participation étant donné le caractere de coordination de la chaîne en croissance. De l'utilisation du sodium et du potassium, il résulte une augmentation significative du type anionique de la chaîne en croissance. Par l'introduction de composé

donneur d'électrons dans le milieu hydrocarboné, la réaction du type anionique devient prédominante dans tous les cas. L'hypothèse d'un mécanisme de coordination anionique pour la polymérisation en présence de composés métalliques organoalcalins est confirmée non seulement par les résultats de l'étude de la structure des polydiènes formés, mais aussi par les données de copolymérisation, obtenues au départ de l'étude de la réaction de transfert de chaîne par ces catalyseurs et même au départ de l'étude spectrophotométrique des composés organométalliques correspondants. Le catalyseur AlR_3-$TiCl_3$ est un autre exemple montrant les caractéristiques spécifiques d'un système de polymérisation catalytique à deux centres. Les études menées à l'aide de ces systèmes, dans la polymérisation de l'éthylène on presence de différents monomères, dans l'homo- et la copolymérisation du styrène et de l'isoprène montrent que le catalyseur est un système à quatre membres déficients en électrons et qui en première approximation est caractérisé par la présence de deux centres: un centre d'absorption qui forme un complexe avec les monomères, et un centre réactionnel ('la racine' de la chaîne en croissance, qui joignent la molécule du monomère sur la chaîne en croissance. Un examen de la copolymérization du styrène et de l'isoprène montre que la séquence de l'union des monomères dans la chaîne polymérique est déterminée par la combinaison de deux actions: la vitesse de réaction dont dépend la nature du monomère et la 'racine' de la chaîne en croissance.

Zusammenfassung

Die Untersuchung der durch Organolithium-, -natrium- und -kaliumverbindungen katalysierten Polymerisation konjugierter Diene ergab, dass diese Reaktionen in Kohlenwasserstoffen als Reaktionsmedium über einen anionisch-koordinativen Mechanismus verlaufen, für den die Teilnahme zweier Zentren, nämlich der metallischen und der Kohlenwasserstoffkomponente der wachsenden Kette, an der Wachstumsreaktion charakteristisch ist. Das Ausmass der Teilnahme des Alkalimetalls an der Wachstumsreaktion nimmt in der Reihenfolge Li > Na > K ab. In Übereinstimmung mit dem koordinativen Charakter des Kettenwachstums ist also die Teilnahme bei den Lithiumverbindungen am stärksten ausgeprägt. Bei der Verwendung von Natrium und Kalium tritt in erheblichem Ausmass eine Wachstumsreaktion vom anionischen Typ auf. Werden dem Kohlenwasserstoffmedium Elektronendonoren zugesetzt, so herrscht in allen Fällen die anionische Reaktion vor. Die Hypothese eines anionisch-koordinativen Polymerisations-mechanismus in Gegenwart von Organoalkalimetallverbindungen wird nicht nur durch die Ergebnisse der Strukturuntersuchungen an den gebildeten Polymeren, sondern auch durch Copolymerisationsdaten, durch die Ergebnisse der mit diesen Katalysatoren durchgeführten Untersuchungen von Kettenübertragungsreaktionen sowie durch die bei der spektrophotometrischen Untersuchung der entsprechenden organometallischen Verbindungen erhaltenen Befunde gestützt. Ein anderes Beispiel für die spezifischen Charakteristika eines Zweizentren-Polymerisationskatalysators, der die Kettenwachstumsreaktion selektiv kontrolliert, ist der Katalysator AlR_3-$TiCl_3$. Die mit diesem System durchgeführten Untersuchungen der Polymerisation von Äthylen in Gegenwart verschiedener Monomerer sowie der Homo- und Copolymerisation von Styrol und Isopren ergaben, dass der Katalysator ein viergliedriges Elektronenmangel-System ist, das in erster Näherung durch zwei Zentren charakterisiert werden kann, nämlich ein Absorptionszentrum, das mit dem Monomeren einen Komplex bildet und ein Reaktionszentrum (die 'Wurzel' der wachsenden Kette, welches das absorbierte Monomermolekül mit der wachsenden Kette verknüpft. Wie aus eingehenden Untersuchungen der Copolymerisation von Styrol und Isopren hervorgeht, wird die Sequenz der Monomereinheiten in der Polymerkette durch das Zusammenwirken der beiden Schritte bestimmt, deren Geschwindigkeit von der Natur des Monomeren under der "Wurzel" der wachsenden Kette abhängt.

Discussion

A. D. Caunt (*I.C.I. Ltd., Herts, Great Britain*): In polymerizations of ethylene with $TiCl_3$-AlR_3 catalysts it is stated in the paper presented that butadiene slows up the reaction. In the resumé read by Dr. Plate, I got the impression that no polybutadiene is formed under these conditions. Could Dr. Plate, state whether such polymer was detected or if a careful search for it had been made?

S. S. Medvedev: In polymerization of ethylene in hydrocarbon media at 25°C. with α-$TiCl_3$–$AlEt_3$ catalysts butadiene and isoprene additives slow up the reaction. But no polybutadiene is formed under these conditions.

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Mechanism of Stereospecific Polymerization of Styrene with Alkali Metal Alkyls

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I. INTRODUCTION

The promotion of the polymerization of styrene by *n*-amylsodium was first observed in 1952 by Morton and Grovenstein.[1] By means of similar tests we discovered in 1957 that under appropriate conditions polymers were formed which in their tacticity were hardly different from those prepared with the typical Ziegler catalysts.[2] Previous investigations indicated that, unlike the case with the alfin catalysts, the method of preparation of amylsodium had no influence on the tacticity of the polystyrene. When catalysts obtained from the reaction of *n*-amyl chloride with metallic sodium ($C_5H_{11}Cl + 2Na \rightarrow C_5H_{11}Na + NaCl$) or preparations for polymerization which were free from inorganic constituents (like NaCl) were used, practically no difference in the effectiveness of these promoters was found. Therefore, it must be concluded that in *n*-amylsodium, unlike the alfin catalysts, the inorganic constituent has no significance upon the reaction mechanism. This follows from the fact that it is immaterial if the sodium is reacted with amyl chloride, bromide, or the iodide. In addition the alkyl residue does not have any significant effect on the stereospecificity of the polymerization reaction, as it can be linear, branched, or arylaliphatic.

On the other hand, shortly after we started our investigations it became apparent that the nature of the surface of the catalyst has a pronounced influence on the course of the polymerization of styrene with *n*-amylsodium. The polymerization temperature and rate also distinctly influence the tacticity of the polymers.[3]

As the result of experimental data which we have gathered in the meanwhile,[4] certain assumptions can be made regarding the mechanism of stereospecific polymerization of styrene with *n*-amylsodium and similar initiators from alkali metallic alkyl compounds.

II. RESULTS

1. Previous Investigations

The polymerizations with amylsodium and similar alkyl compounds of elements of the first group in the Periodic Table (with the exclusion of

lithium) were carried out as described in previous papers, that is, in heterogeneous medium in hexane, heptane, or toluene.[3] The polymerization temperature has a significant bearing upon the stereospecificity of the reaction. With organosodium compounds only poorly crystallizable polystyrene was obtained at temperatures of 0°C. and above, whereas, at temperatures of −20 to −30°C. polymers were produced which in their crystallinity were hardly differentiable from those products obtained with trialkylaluminum–titanium halide mixed catalysts. Again, with polymerization at sufficiently low temperatures practically no atactic portion can be extracted from the products with boiling *n*-heptane, the extractable part increasing with a rise in polymerization temperature. The crystallinity and softening point of the nonextractable polymers decrease simultaneously.

Potassium, cesium, and rubidium alkyls behave alike when used as polymerization initiators; *n*-amylpotassium, *n*-octylpotassium, *n*-hexadecylpotassium, and benzylpotassium all produce tactic polystyrene. However, an astonishing fact is that to achieve the same stereospecificity, the polymerization in *n*-hexane must be conducted in a temperature range of −60 to −70°C. with potassium initiators; in the case of dodecylrubidium, a lower temperature (−80°C.) is necessary, whereas with *n*-amylsodium a temperature of only −20°C. is required. The decrease in stereospecificity runs parallel with the increase in polymerization rate as temperature rises.

The degree of tacticity of the crystalline products may be evaluated by melting points and x-ray diagrams.

2. Copolymerization of Styrene with Methyl Methacrylate

It has already been mentioned in an earlier work[5] that the heterogeneous polymerization of methyl methacrylate with alkali alkyl compounds results in the formation of polymers having very different tacticities, depending upon the temperature and solvent employed. In the copolymerization of a mixture of styrene and methyl methacrylate with radical initiators a real copolymer consisting of both monomers is obtained; however, with an anionic polymerization a pure polymethyl methacrylate is nearly always formed, because the styrene ion can promote the polymerization of methyl methacrylate but the methyl methacrylate ion does not start the polymerization of styrene.[6] In our copolymerization investigations with *n*-amylsodium in heptane at a temperature of −30°C. the yield increases linearly with the rise in the concentration of methyl methylacrylate in the monomer mixture, which indicates the formation of almost pure polymethyl methacrylate (Fig. 1). The infrared spectra of the polymerizates correspond extensively to the spectra of isotactic polymethyl methacrylate. Only at 14.25 μ is it possible to recognize the wagging vibration of the benzene nucleus in products obtained when the styrene content in the monomer mixture is more than 70 mole-%. Thus it can be ascertained from the intensity of the band that less than 1 mole-% styrene units are incorporated

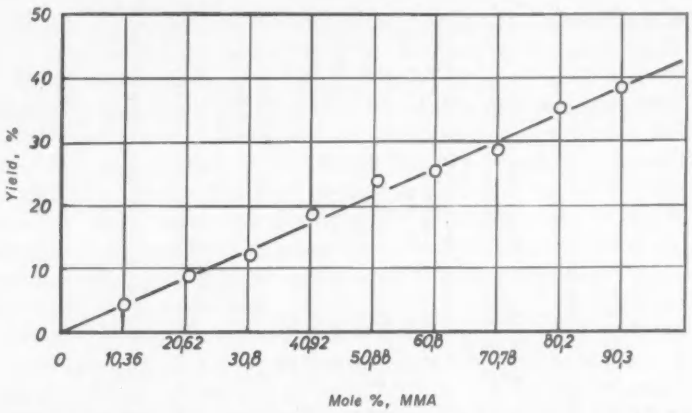


Fig. 1. Yield vs. MMA content in monomer mixture for copolymerization of styrene and methyl methacrylate (MMA) with *n*-amylsodium in *n*-heptane at −30°C.

into the polymer.[7] Therefore the copolymerization investigations indicate an anionic polymerization mechanism, because by radical or cationic polymerization the incorporation of styrene can be clearly established.

3. Polymerization with Optically Active 2-Methylbutylsodium

Murahashi and co-workers[8] have already polymerized styrene with optically active 2-methylbutylsodium. However, the isotactic polystyrene so obtained showed no unusual character and was quite identical with that obtained by an inactive catalyst. We carried out similar tests to examine the possibility of inducing an asymmetric chain initiation by means of an optically active catalyst, that is, to favor a chain configuration in the initiating step. However, the polymers thus obtained possessed only small rotation values in polarized light. The polymerization conditions and the properties of the polymerizates are compiled in Table I. The tacticity of the crystalline isotactic polystyrene fractions corresponds to the tacticity of polymerizates prepared with the help of *n*-alkyl sodium. The rotation measurements of the polymerizates prepared with optically active catalysts were carried out in a benzene solution in 2 dm. and 4 dm. polarimeter tubes. For the measurement of small values of rotation it was necessary to investigate and eliminate systematically all sources of error.

The specific rotation of polymerizates produced by optically active catalysts is very small; for example, in the heptane insoluble polystyrene portion (samples P 27 Kr, P 29 Kr) the values lie on the boundary of detectability. Only with the heptane-soluble portions (samples P 25 KD, P 27 KD, P 29 KD) could values be measured with an error of only 10%. The reality of these values confirmed the observed rotation dispersion (OM 12-P 27 KD).

To evaluate the specific rotation it was necessary to calculate the in-

TABLE I
Rotation Measurements of Polystyrene Prepared with Optically Active 2-Methylbutylsodium[a]

Test no.	Polystyrene no.[b]	Concentration p, g./100 ml.	Thickness of layer d, dm.	$\Delta\alpha$ (= ±0.007), degrees	$[\alpha]_D^{20}$ (= α 100/dp), degrees	Molecular weight $M\eta$	Endgroup rotation α_E	$\frac{\alpha}{\alpha_E}$
OM 12	P 27 KD	4.683	2	+0.064	+0.68 ± 11%	5,400	0.048	1.3
OM 13	P 27 KD	4.985	4	+0.120	+0.60 ± 4%	5,400	0.102	1.2
OM 15	P 29 KD	4.228	4	+0.097	+0.57 ± 5%	4,700	0.099	1.0
OM 9	P 27 Kr	2.930	2	+0.011	+0.19 ± 64%	28,800	0.006	2.0
OM 14	P 29 Kr	2.630	4	+0.003	+0.03 ± 100%	23,400	0.012	(0.25)
OM 12	P 13/1 KD[c]	4.788	2	+0.008	—	4,800	—	—
OM 13	P 13/1 KD	5.095	4	+0.008	—	4,800	—	—
OM 12	P 27 KD	4.683	2	+0.057	+0.61 ± 12%		(λ = 650 mμ)	
OM 12	P 27 KD	4.683	2	+0.082	+0.88 ± 9%		(λ = 530 mμ)	
OM 12	P 27 KD	4.683	2	+0.103	+1.10 ± 7%		(λ = 470 mμ)	

[a] Wavelength = 589 mμ (Na_D line); solvent = benzene (p.a., Merck). For every measurement 27 readings were taken; the average error of individual measurements was ±0.005°.

[b] KD = heptane-soluble, amorphous atactic portions from P 27 and P 29 obtained from solution by crystallization in boiling *n*-heptane; Kr = heptane-insoluble, crystalline isotactic portion from P 27 by the crystallization in boiling *n*-heptane.

[c] Prepared with *n*-amylsodium.

fluence of the addition of 2-methylbutyl groups on the monomeric styrene which is possible in the initiation step. As basis for the calculation of the endgroup effect, the specific rotation value of an optically active hexylbenzene[9] CH_3–CH_2–$HC(CH_3)$–CH_2–CH_2—C_6H_5, was used; this served as a model substance for the polymer. It was assumed that during the initiating step the addition of the 2-methylbutyl groups took place at the α-position of styrene. However, it is known that with n-butyllithium the butyl residue is bonded at the β-position of the styrene. It can be presumed that the specific rotation of the optically active hexylbenzene is not very different from that of a corresponding heptylbenzene. Literature values are not available here.

The calculation is based upon the following relation, where α_E is the rotation due to optically active endgroups, α_H is the rotation of the pure optically active hexylbenzene ($[\alpha]_D^{20} = +17.1°$), E is the fraction of endgroups, which is the ratio of the molecular weight of hexylbenzene (162.16) to that of polystyrene (M_η), d is the layer thickness in decimeters, and p is the concentration in grams/100 ml. solvent.

$$\alpha_E = \alpha_H E$$

$$\alpha_H = [\alpha]_D^{20}\, dp/100$$

$$E = 162.16/M_\eta$$

Thus

$$\alpha_E = \frac{17.1\, dp \times 162.16}{100 M_\eta}$$

$$\alpha_E = +27.7\, dp/M_\eta$$

The values of α_E calculated according to this for the endgroups are indicated in column 8 in Table I, and in column 9 the quotients from the measured rotations α of the polymers of styrene and the calculated α values for the end groups. The α/α_E ratio for optically active polymers soluble in heptane is 1.1, while most higher molecular isotactic polymers of styrene, which are insoluble in heptane, give very fluctuating values.

Two factors have to be considered which influence the quotient α/α_E. Firstly, the catalysts were only up to 85% optically pure, therefore about 15% of the endgroups incorporated into the polymers come from the optically inactive catalyst. Secondly, for the evaluation of α_E the factor M_η would be necessary. However, M_η is not known exactly; the estimated value of M_η/M_n is 1.5.

The influence of both these factors decreases simultaneously and extensively in the calculation of α_E.

When both these mentioned factors are considered the above given value for the average α/α_E for the heptane-soluble portions is lowered from 1.1 to about 0.9. It can therefore be assumed that the ratio α/α_E for the heptane-soluble portions is approximate unity.[11]

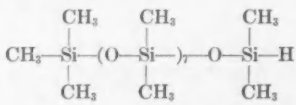
It follows that the activity of polystyrene produced by optically active isoamylsodium does not exceed the optical activity which is due to the endgroup effect.

An asymmetric induction apparently did not occur by the polymerization or is not detectable due to failure in the asymmetry of adjacent regions in the middle segments of the macromolecule.

4. Investigation to Detect Unsaturated Endgroups in Tactic Polystyrene

The above mentioned tests dealt with polymerization with optically active initiators yielding one known endgroup in the polymer chain but up to now nothing has been known regarding the other endgroup. Therefore, investigations were then undertaken to ascertain if after precipitation in methanol the polymer contained unsaturated endgroups. For this purpose by means of infrared spectroscopy compensation of a high molecular polystyrene—which is certainly free from double bonds—with low molecular isotactic polystyrene was attempted in order to detect double bonds in the latter. This should have produced differences in the infrared spectra, for example, at 6.1 μ, as the C=C valence vibrations (which can also be caused by vinyl and vinylidene groups) occur here. However, even with low molecular polystyrene (molecular weight about 5000) no unsaturated endgroups were determinable by this method.[11]

Also the addition of an oligomeric siloxane monohydride



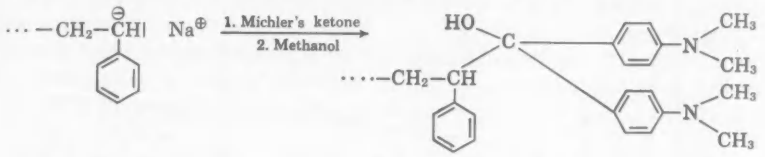
to the existing C=C bonds according to Greber and Metzinger[12] was unsuccessful. The analytic determination of carbon in the reaction products produced constant values which, within experimental error, excluded an addition of siloxane monohydride on the investigated polymers. On the other hand, the expected values were obtained with model tests carried out on other polymers with known double bond content, so that an error in the method does not exist.[11]

5. Termination of Active Polymers with Michler's Ketone

Although unsaturated endgroups could not be determined in tactic polystyrene produced by hetereogeneous alkali organic initiators, it was found that Michler's ketone reacted with the active polymers. The principles of these investigations are in a paper by Trotman and Szwarc[13] who terminated "living polymers" with Michler's ketone, thereby determining the number of active endgroups.

It can be assumed that during the polymerization of styrene with *n*-amylsodium the active end of a macromolecule exists as an organometallic compound. By the reaction with Michler's ketone a diarylalkylcarbinol is formed which is easily convertible into the corresponding colored

salt with ferric chloride in tetrahydrofuran.[13] This colored salt is relatively stable and can be quantitatively photometrically evaluated.



Investigations on model compounds showed that the extinction coefficient at 6.25 mμ (ϵ = 6000 ± 1000 l./mole cm.), as calculated by Trotman and Szwarc for "living" polymers terminated by Michler's ketone in an analogous manner in tetrahydrofuran/$FeCl_3$ was also applicable in our case.

Tactic polymers obtained with *n*-amylsodium were terminated directly with Michler's ketone at a temperature of −20°C. after a definite polymerization period. After removal of excess Michler's ketone the tactic polymers were purified and dissolved in tetrahydrofuran containing 0.01 mole/l. $FeCl_3$ and spectroscopically investigated.

From the extinction results of the obtained polystyrene the number-average molecular weight M_n can be derived when an extinction coefficient of 6000 l./mole cm. for the diarylalkylmethyl colored salt is taken.

The ratio of the viscometric molecular weight, M_η to the number-average molecular weight M_n is taken as the criterion for the polymolecularity of the polymers terminated with Michler's ketone. Taking into consideration the yields the quotient M_η/M_n for the terminated polymers corresponds to that obtained for polymers prepared with *n*-amylsodium and terminated by other means.

From these results it can be concluded that during the polymerization of styrene with *n*-amylsodium the initiated chains remain to a great extent active (approx. 70–100%). This agrees well with the results obtained from the determination of the double bonds, in which no double bonds could be determined in polymers prepared with *n*-amylsodium or 2-methylbutylsodium. Only when the number-average molecular weight of the polymers is known can more precise values be obtained. Detailed investigations are in progress which deal with the exact determination of the second endgroup in polymers prepared with *n*-amylsodium.

III. DISCUSSION

The fractionation of polymers prepared with *n*-amylsodium, yielded distribution curves showing a sharp maximum by relatively small molecular weights in their differential mass distribution function (see Fig. 2). The nonuniformity of these polymerizates is large and appears to be dependent upon the yield and the polymerization temperature. Detailed investigations into the conditions of crystallization indicated that particularly with the low molecular fractions a considerable amount of atactic polystyrene was found with the isotactic polymer. Hence, the apparent

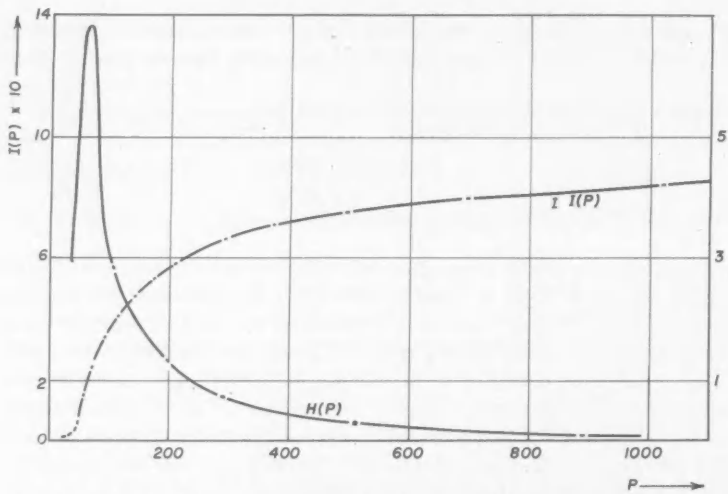


Fig. 2. Mass distribution curves of polystyrene obtained with *n*-amylsodium at −20°C. (0.96 mole styrene, 0.078 mole *n*-amylsodium, 1000 ml. *n*-hexane, 6 hr., yield 16.1%).

poor tacticity of the lowest fractions is caused by the admixture of atactic materials.[11] Accordingly, during the polymerization of styrene with *n*-amylsodium at temperatures from −20°C. two reactions occur: one leads to the formation of tactic polystyrene with relatively high molecular weights, while the other one results mainly in the formation of atactic, low molecular polymers. In the middle molecular weight range (10,000–20,000) there exists a mixture of atactic and isotactic polymers, which with present methods cannot be separated with certainty.

The reason for the formation of low molecular polystyrene cannot at present be clearly explained. Possibly their propagation starts on regions on the surface of the catalyst, which due to spatial reasons do not allow a steric orientation of the monomer during the propagation phase.

Perhaps they were also formed by side reactions in the solvent, perhaps by metals transfer on styrene and the formation of styrene anions, or from the sodium in the catalyst or direct with amylsodium. The already mentioned comparatively sharp maximum in the differential mass distribution curve, which lies mostly between degrees of polymerization of 50 and 100 supports these arguments. The appearance of this maximum is similar to a maximum of a distribution curve for typically anionically prepared "living" polymers.

The interesting main reaction is without doubt responsible for the stereospecific polymerization. No definite conclusions can be made regarding the actual reasons for the stereoregulation. However, previous investigations[3] have shown distinctly that the stereospecific polymerization must take place on the surface of the catalyst. With progressive conver-

sion, the crystallinity of the produced polystyrene decreases without significantly altering the molecular weight. On the other hand, if the amount of catalysts and thus the effective surface area is increased and the reaction conditions are kept the same, the crystallinity of the polymerizate remains constant up to a considerably higher conversion. The effect can be explained as due to the deposition of the stereoregular polymer on the surface of the catalyst, which after a definite conversion is covered by the resulting polymer.

The influence of the polymerization rate is important. Generally, tacticity decreases with an increase in reaction rate as shown by a lowering of stereospecificity with rise in polymerization temperature, and further by transition from a pure nonpolar solvent, hexane, to polar systems, perhaps by addition of toluene or ether. Hereby, polarization of the alkyl–metal bond as well as the rate of polymerization increases. At the same temperature, polymerization in toluene proceeds more rapidly than in *n*-hexane, with the tacticity of polystyrene decreasing with a rise in the polymerization rate. By decreasing the polymerization rate, that is, by lowering the temperature, good crystallizable polystyrene is obtained, even when toluene is used. In this case, the resulting polymer is dissolved and the catalyst is the only heterogeneous part, whereas in hexane, the polystyrene is insoluble throughout polymerization.

The mentioned copolymerization investigations with methyl methacrylate indicate that the polymerization with sodium alkyls proceeds by means of an anionic mechanism. The tests carried out with optically active isoamylsodium showed that the initiation step involves formation of alkyl anions. It can be assumed that the anions are derived from the surface of the catalyst. Depending upon the polymerization medium employed during the propagation process the polymer chains with alkyl residues as endgroups are immersed in the solvent or remain on the surface of the catalyst and gradually cover it. In this case, the apparent tacticity

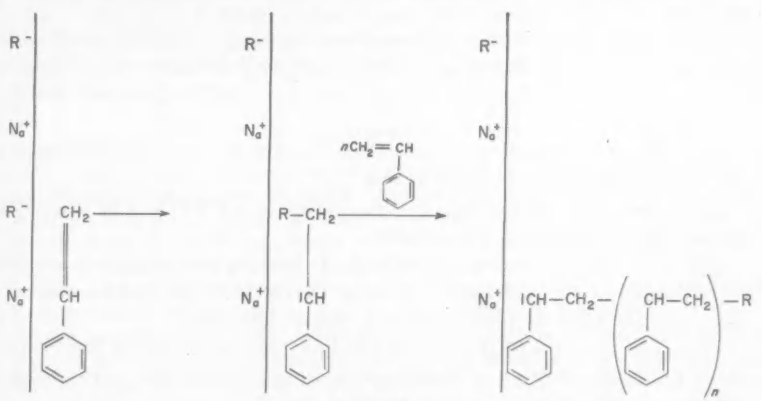


Figure 3.

decreases with increase in conversion, as the polymer chains which are formed later are not so well arranged sterically. This could also explain the occurrence of the atactic polymers which were separated by fractionation as relatively low molecular products and could not be crystallized.

The initiation and propagation steps can be represented schematically as shown in Figure 3.

This hypothesis could also explain the stereoregulation on the surface of the catalyst and also the incorporation of an endgroup from the catalyst into every macromolecule.

In contrast, a general formulation for the termination reaction cannot be given. The investigations with Michler's ketone as terminating agent show that the majority of the growing chains exist in an active state to the end of polymerization, that is, until the polymerization is stopped by a terminating agent. The heterogeneous nature of the polymerization, in which the steric conditions are of extreme importance, accounts for the fact that no narrow molecular weight distribution was obtained as is customary for "living" polymers. The scheme suggested by Szwarc and co-workers[14] for "living" polymers involving the termination of the growing chain by a hydride transfer according to present results is not applicable in our case. According to Szwarc, double bonds should be determinable at least in the low molecular polymers:

$$-CH_2-\overset{\ominus}{C}H(C_6H_5)\,|\,\overset{\oplus}{N}a \rightarrow -CH=CH(C_6H_5) + NaH$$

Such a hydride transfer is hardly possible because it has been shown[7] that complex hydrides like lithium aluminum hydride, sodium borohydride, or potassium borohydride have no influence on the polymerization of styrene with *n*-amylsodium in *n*-heptane. Hence, they are not effective as chain transfer agents and also they have no influence upon the tacticity of the polymers.

From these results it is possible to summarize the following conclusions dealing with the mechanism of the stereospecific polymerization of styrene with *n*-amylsodium and other similar insoluble alkali organic polymerization initiators.

(*1*) The stereospecific polymerization of styrene with *n*-amylsodium is a heterogeneous anionic polymerization.

(*2*) The initiation step involves formation of alkyl anions of the initiator on the solid surface of the catalyst.

(*3*) The polymers contain practically no unsaturated endgroups, so that termination of the individual growing chains through hydride transfer does not take place or at the most to a very small extent.

(*4*) The majority of the initiated polymer chains maintain their active state until the addition of foreign substances (water, etc.), presenting a type of insoluble "living" polymers.

(5) The stereoregulation follows by orientation of the growing chains

on the solid surface of the catalyst, the orientation demanding, thereby, a definite time. When the rate of polymerization is too high, the tacticity is poor. The tacticity can be improved by lowering the temperature and therefore the rate of polymerization.

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Synopsis

Alkyl compounds of sodium, potassium, rubidium, and cesium promote the stereospecific polymerization of styrene in aliphatic hydrocarbons. Being insoluble, all these catalysts were effective in heterogeneous systems. Therefore the surface of the heterogeneous initiators plays an important role in polymerization. It can be assumed that the polymerization with alkali metal alkyls is of an anionic nature, whereby the steric regulation depends upon the orientation of the adding monomer on the solid surface of the catalyst. In polymerizations with optically active alkali alkyls one optically active endgroup per macromolecule can be determined in polymers with not too high molecular weight. Therefore it is concluded that the polymerization is started by the alkyl anion of the catalyst. The growing polymer chains can be terminated with Michler's ketone. The amount of incorporated ketone indicates that most of the growing chains are "living" during the whole polymerization time. This is in agreement with the fact that no unsaturated endgroups can be found in polystyrene obtained with alkali organic catalysts.

Résumé

Les composés alcoylés du sodium, du potassium et du césium permettent la polymérisation stéréospécifique du styrène dans les hydrocarbures aliphatiques. Etant insolubles, tous ces catalyseurs sont en fait des systèmes hétérogènes. C'est pourquoi la surface des initiateurs hétérogènes joue un role important dans la polymérisation. Il peut être admis que la polymérisation par des dérivés alcoyl-métalliques est de nature anionique, où la régulation stérique dépend de l'orientation du monomère additionné à la surface solide du catalyseur. Lors de la polymérisation par des dérivés alcoyl-métalliques optiquement actifs on forme une seule extrémité optiquement active par molécule de polymères si le poids moléculaire n'est pas trop élevé. C'est pourquoi on conclut que la polymérisation débute par l'anion alcoylé du catalyseur. La chaîne polymérique en croissance peut être terminée oar la cétone de Michler. Au départ de la quantité de cétone incorporée, il résulte que la plupart des chaînes en croissance

restent en vie au cours de toute la durée de la polymérisation. Ceci est en accord avec le fait qu'on ne trouve pas d'extrémité de chaîne insaturée dans le polystyrène obtenu par des catalyseurs organoalcalins.

Zusammenfassung

Natrium-, Kalium-, Rubidium- und Cäsiumalkyl-verbindungen bewirken eine stereospezifische Polymerisation von Styrol in aliphatischen Kohlenwasserstoffen. Da alle diese Stoffe unlöslich sind, bilden sie heterogen-katalytische Systeme. Es spielt daher die Oberfläche der heterogenen Starter eine wichtige Rolle bei der Polymerisation. Man kann annehmen, dass die Polymerisation mit Alkalimetallalkylen anionischen Charakter besitzt, wobei die sterische Regelmässigkeit von der Orientierung des herantretenden Monomeren an der festen Katalysatoroberfläche abhängt. Bei der Polymerisation mit optisch aktiven Alkalialkylen kann bei Polymeren mit nicht zu hohem Molekulargewicht eine optisch aktive Endgruppe pro Makromolekül festgestellt werden. Daraus folgt, dass die Polymerisation durch das Alkylanion des Katalysators gestartet wird. Die wachsenden Polymerketten können mit Michler's Keton abgebrochen werden. Aus der Menge des eingebauten Ketons ergibt sich, dass sich die Lebensdauer der Mehrzahl der wachsenden Ketten über die ganze Polymerisationsdauer erstreckt. Das stimmt mit dem Umstand überein, dass in dem mit alkaliorganischen Katalysatoren erhaltenen Polystyrol keine ungesättigten Endgruppen nachgewiesen werden können.

Discussion

Dr. Eroussalimsky (*Léningrad, U.R.S.S.*): (*1*) How varies the polymerization rate with the nature of catalyst?

(*2*) Is any connection not found between the polymerization rate and stereoregularity of the polymers?

Dr. Braun: (*1*) At the same temperature the polymerization rate increases using catalysts with the same alkyl group and different metals in the following order: Na < K < Rb < Cs.

(*2*) In the case of the polymerization of styrene with amyl sodium the stereoregularity of the polymers increases decreasing the polymerization temperature from room temperature to −40°C.; further lowering of the temperature has no significant effect on tacticity.

Dr. Y. Y. Tan (*Delft, Hollande*): (*1*) Did you find the presence of NaCl in your alkylsodium-compounds to be necessary for their stereospecificity with regard to the polymerization of styrene?

(Answer was no.) Comment: It would be reasonable to expect that the presence of NaCl in the organosodium compounds would be determined to the stereoregularity power because of the distortion of the crystal lattice of alkylsodium by NaCl.

(*2*) Have you utilized aromatic sodium compounds for the polymerization of styrene?

(Answer was yes, but the polymerization rate is slower than by using the alkyl derivatives; moreover the stereospecificity was also lower.) Comment: Although we also did find the alkaryl sodium compounds to be much less effective catalysts we however found a somewhat higher stereoregularity effect, e.g., with triphenylmethylsodium in comparison to *n*-amyl sodium.

D. Braun: (*1*) Also *n*-amylsodium prepared from diamyl mercury and sodium yields tactic polystyrene. This catalyst was absolutely free of NaCl or other inorganic constituents (see *Makromol. Chem.*, **36,** 232 (1960)).

(*2*) We made no detailed investigations with triphenylmethylsodium but in a few experiments we obtained similar results.

T. Tsuruta (*Kyoto, Japan*): I think there is few research concerning the catalyst composing of Rb and Cs. How about the stereoregulating behaviors of the Rb and Cs compounds?

Dr. Braun: There is little difference in the stereoregulating ability of these alkali metal compounds compared with Na and K compounds.

M. Farina (*Milan, Italie*): I think that the use of optically active catalysts in order to determine the amount of terminal groups has too low a sensitivity to give good results.

But if one wants to see, with these catalysts if there is an asymmetric induction, it is necessary to use monomers to give enantiomeric chains. This is not the case of styrene.

D. Braun: We used optically active catalysts because we were not in the position to work with labelled initiators; of course the sensitivity of our method is rather low, but not too low for polystyrene of a molecular weight, which is not too high. We did not expect to have an asymmetric induction of the styrene polymerization with optically active catalysts.

M. Osgan (*Institut Français de Petrole, France*): You indicated that in order to obtain high isotacticity with organo-rubidium compounds, as initiators, it is necessary to reduce the temperature of polymerization far below the temperature when organo-sodium compounds are initiators. On the other hand (with organosodium initiators) the crystallinity of the polymers decreases with conversion.

I wonder whether this decrease of crystallinity with conversion and the need to decrease the polymerization temperature, when using organo-Rb instead of organo-Na, both cannot be better explained by a site-exchange mechanism of essentially non-terminating polystyrene chains, as already found by Natta in case of polypropylene?

Dr. Braun: In our case we have no indication for such a reaction. If we polymerize to high conversions at very low temperature (where at 10% conversion we have only tactic polystyrene) only a part of the obtained polystyrene is of high tacticity. We think that this is a result of covering the stereoregulating surface of the catalyst with the polymer.

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Determination of Active Centers in Stereospecific Diene Polymerization

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INTRODUCTION

The nature and concentration of active centers, the rates of growth, and possible transfer and termination reactions in coordination polymerization are of considerable interest. In this communication the kinetics of the polymerization of isoprene by the $VCl_3/AlEt_3$ catalyst system are described particularly from these standpoints. Estimates are made of the concentrations of polymer molecules linked to metal atoms by terminating the reactions with tritiated methanol. Similar methods have been employed already in studies of the polymerization of ethylene,[1] propylene,[2,3] and methyl methacrylate.[4] The influence of electron donors, including amines, thioethers, ethers, and a phosphine, has been examined.

EXPERIMENTAL

Materials

The solvent used was SBP5 (Shell Chemicals Ltd.) b.p. 90–105°C., a mixture of paraffins (66%), naphthenes (30%), and aromatics (4%). It was purified by washing with concentrated sulfuric acid and then with water, after which it was distilled and dried over alumina.

Isoprene was distilled, dried over alumina and stored at −20°C. to prevent dimerization. Moisture contents were determined by a method to be described[5] and found to be in the region of 10 ppm.

Isopropyl ether was washed with alkali to remove inhibitor, and most of the water then removed by azeotropic distillation under reflux. This was followed by distillation and drying over alumina. Other additives were purified, usually by distillation, and were also dried over alumina.

Triethyl aluminum having the composition 82% triethyl aluminum, 15% tributyl aluminum, 2% aluminum hydride, and 1% aluminum ethoxide was used without further purification. The vanadium trichloride was pumped out under high vacuum to remove $VOCl_3$ and other volatile impurities. Tritiated methanol was prepared from methanol by exchange with tritiated water in the presence of sodium hydroxide. It was purified by distillation.

To dispense with minimum contamination the small quantities of VCl_3 required for polymerizations the dispenser shown in Figure 1 was used. Vanadium trichloride was placed in tube A under an atmosphere of dry nitrogen in a dry-box, and then pumped under a high vacuum through B. Throughout this process the plunger C maintained a tight seal at D. A weighed ampule E, made of thick-walled glass tubing, a thin, easily broken end F, and a B14 socket at the top, was fitted to the B14 cone at the lower

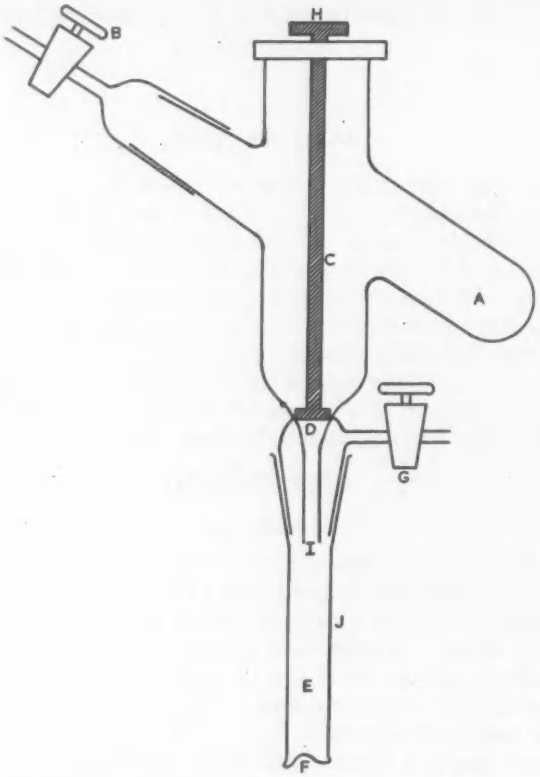


Fig. 1. Apparatus for ampuling vanadium trichloride.

end of the dispenser, was flamed out and evacuated through G. Vanadium trichloride was tapped down onto D and the plunger unscrewed at H, lifting it at D and allowing a small quantity to fall through the tube I into the bottom of the ampule. The seal at H was made by a Viton A rubber diaphragm. D was closed and the ampule was sealed off at J. To obtain the weight of VCl_3 the sealed socket was replaced by a fresh ampule under dry nitrogen in the dry-box and then weighed together with the sealed ampule.

Examination of Soluble Components of Catalyst Systems

The apparatus used is shown in Figure 2. A and B were reservoirs containing the electron donor and a petrol solution of $AlEt_3$, respectively, both having been degassed under high vacuum. Ampule C, containing a known weight of VCl_3, was placed in the reactor D, and with valve E open the system was evacuated through F, pumping for several hours. With the tap

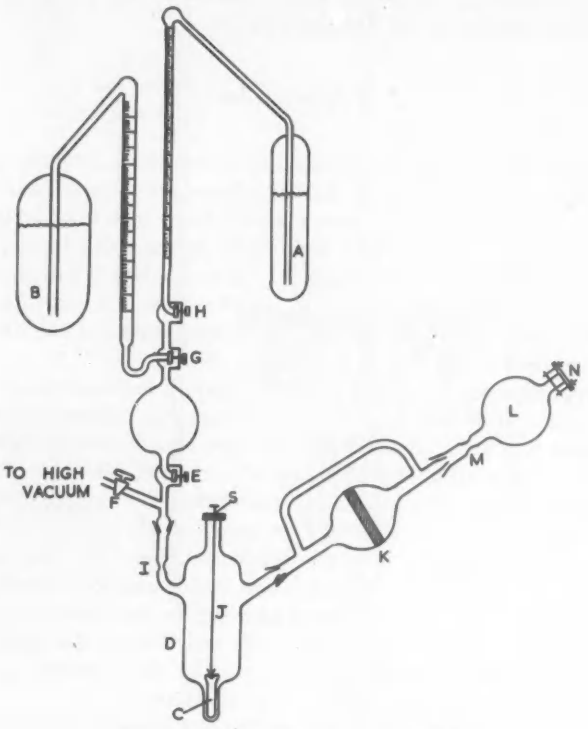


Fig. 2. Apparatus for catalyst analysis.

F closed, the Springham valves E, G, and H were used to introduce known quantities of $AlEt_3$ solution and the electron donor into the reactor. The reactor was then sealed off at I and the ampule broken with the stainless steel rod J, fitted through a high vacuum rotary seal (Edwards, type C607) S. After shaking for 30 min. the apparatus was tilted and the supernatant liquid was filtered through the sinter K into the receiver L which was sealed off at M. One end of the receiver, N, was closed with a Neoprene/Butyl self-sealing rubber gasket through which it was flooded with dry nitrogen and samples withdrawn with a hypodermic syringe and placed in weighed stoppered flasks. This latter procedure was carried out in the

nitrogen atmosphere of a dry-box. Measurements (at room temperature) were carried out at concentration levels well above those used normally for a polymerization reaction, in order to magnify any differences in composition of the liquid phase.

Aliquots were analyzed for Al, V, and Cl. The $AlEt_3$ was decomposed by slow addition of methanol, redissolved with dilute H_2SO_4, and the hydrocarbon layer evaporated off. Aluminum was determined volumetrically with EDTA/$ZnSO_4$. Vanadium was estimated by the phosphotungstate method and chlorine by the Volhard titration.

Polymerization

Most experiments were carried out in the apparatus shown in Figure 3, which allowed the progress of the polymerization to be followed dilatometrically. The mercury side arm was sufficiently high to offset the excess pressure of the reactants. The main vessel A was a Q.V.F. $1^1/_2$ in. tube having a Teflon insert in the top seal B. The top plate C was of mild steel and the stirrer was made from $^1/_8$ in. stainless steel rod. A rotary seal S (Edwards type C607) was used and the reactor stirred at ca. 200 rpm by a variable speed motor D with flexible drive shaft.

The apparatus was assembled with the ampule E in place with mercury as a lower seal. After flushing the reaction vessel with nitrogen the reactants were added to a total volume of 175 ml. from a graduated syringe through the aperture F. $AlEt_3$ in SBP 5 was added under nitrogen. The aperture was then closed by a rubber self-sealing gasket. Further mercury was run in from the reservoir G with a hypodermic needle inserted at F to allow residual gases to escape; after its withdrawal the vessel was completely sealed with no gas space. The reaction vessel was then immersed in a thermostat at 50°C., and after about 1 hr. the reaction was started by raising the stirrer so as to break the ampule and liberate the vanadium trichloride. The polymerization was followed by observing the contraction of the mercury in the capillary I with a cathetometer.

To stop the reaction, radioactive methanol was added in excess through the seal at F by use of a hypodermic syringe. After stirring for 1 hr. the vessel was cooled and the polymer solution removed through the seal at H. The apparatus was dismantled to obtain the remainder of the polymer and the whole washed with inactive methanol. It was then purified by dissolving in benzene, washing with a small quantity of dilute ammonia to precipitate catalyst residues, and centrifuging at 3000 G. An aliquot taken for radioactive assay was centrifuged at 25,000 G, reprecipitated by methanol, redissolved in benzene and finally isolated by freeze drying. This removed all traces of active methanol. In treating the data the expansion of the reactants from 20–50°C. was taken to be 4.2% and the density of *trans*-polyisoprene in solution at 50°C. as 0.895 g. $ml.^{-1}$, corresponding to 23.9% volume decrease (on monomer) for 100% conversion.

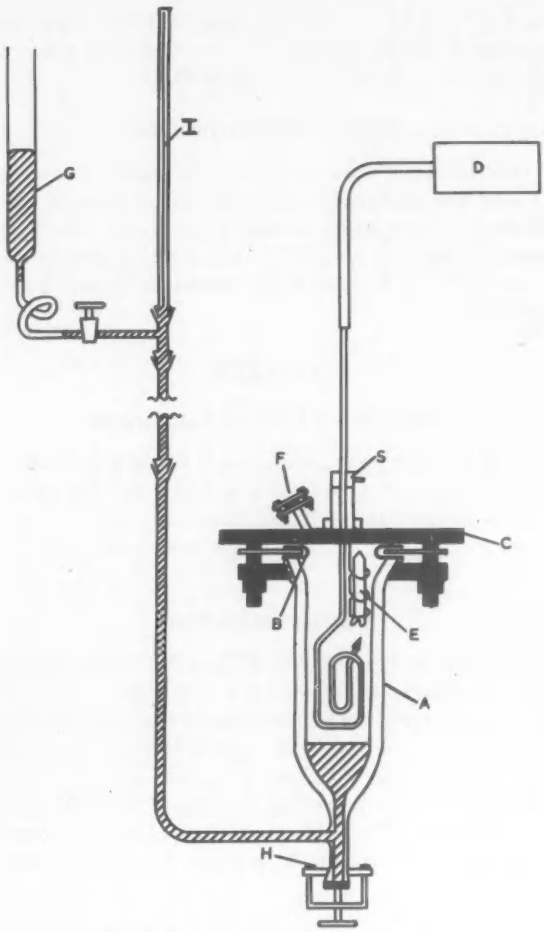


Fig. 3. Polymerization dilatometer.

Radioactive Assay

The method of Bevington and Eaves was used,[6] in which the polymer is combusted and the water so formed reacted with calcium carbide to produce acetylene, which is assayed. Activities (C) were expressed in counts min.$^{-1}$ mg.$^{-1}$ acetylene.

When calculating the specific activities of the original compounds, it was necessary to take into account the different dilutions of hydrogen in acetylene, methanol, and the polymer. The following conversion factors apply to calculations of specific activities from the activities C: Methanol (in counts min.$^{-1}$ mole^{-1}) $5.20 \times 10^4 C$, polyisoprene and polybutadiene (in

counts min.$^{-1}$ g.$^{-1}$), 1.53×10^3C and 1.45×10^3C, respectively. Four different samples of MeOT, having activities within the range 1×10^{10} to 5×10^{10} counts min.$^{-1}$ mole^{-1} were employed.

Polymer Characterization

Rates of crystallization were measured dilatometrically at several temperatures. This was preferred to infrared spectra as being more sensitive to small differences in structure at high *trans* levels. Intrinsic viscosities were measured in benzene at 32°C. Osmotic measurements were made in benzene at 28°C. in Pinner-Stabin osmometers with Ultracella filter "feinst" membranes.

RESULTS

Interaction of Catalyst Components

No vanadium or any appreciable amount of chlorine could be detected in the supernatant liquid above the catalyst. By difference of analysis of supernatants the amount of $AlEt_3$ adsorbed was found to be 0.025 to 0.10 moles per mole VCl_3. These findings were not changed by the addition of an electron donor.

Polymerization Data

All the data refer to the isoprene–VCl_3–$AlEt_3$ system at Al/V ratios of 2/1 except where otherwise indicated.

In Tables I and II are given kinetic data for the unmodified and modified catalysts, respectively. (Here R_f, N_f, and $[M]_f$ refer to the polymerization rate, metal–polymer band concentration, and monomer concentration, respectively, at the termination of the reaction.) Table III gives molecular weight data from some of the polymers; values of M_T are molecular weights calculated from the activity of the polymer by tritium assay, while M_n

TABLE I
Polymerization of Isoprene by VCl_3–$AlEt_3$

$[VCl_3]$, g. l.$^{-1}$	Monomer concentration, mole l.$^{-1}$		Polymerization rates, mole l.$^{-1}$ sec.$^{-1}$ $\times 10^5$		$N \times 10^4$, mole l.$^{-1}$	$R_f/N_f[M_f] \times 10^2$, l. mole^{-1} sec.$^{-1}$	$R_m/[VCl_3][M_0] \times 10^3$, l. mole^{-1} sec.$^{-1}$
	$[M_0]$	$[M_f]$	R_m	R_f			
0.80[a]	1.89	1.79	0.95	0.51	0.48	5.9	0.99
1.07[a]	1.96	1.88	0.70	0.68	0.26	13.9	0.53
1.14[a]	2.52	2.42	1.19	1.19	0.23	21.7	0.65
1.36[a]	1.27	1.16	0.75	0.41	0.72	4.9	0.68
1.56[a]	1.87	1.73	0.97	0.89	0.85	6.1	0.52
2.18[a]	1.85	1.76	0.77	0.42	0.68	3.5	0.30

[a] Different batches of VCl_3.

TABLE II. Effect of Electron Donors on the Polymerization of Isoprene by VCl_3–$AlEt_3$

Additive	[Additive] / [VCl_3]	[VCl_3], g. l.$^{-1}$	Monomer concentration, mole l.$^{-1}$ [M_0]	[M_f]	Polymerization rates, mole l.$^{-1}$ sec.$^{-1}$ $\times 10^5$ R_m	R_f	$N \times 10^4$, mole l.$^{-1}$	$R_f/N_f[M_f] \times 10^2$, l. mole^{-1} sec.$^{-1}$	$R_m/[VCl_3][M_0] \times 10^3$, l. mole^{-1} sec.$^{-1}$
Tetrahydrofuran	2.0	2.07	1.85	1.68	1.51	0.91	3.40	1.6	0.62
Tetrahydrofuran	6.0	1.72			No polymerization				
Diethyl ether	3.0	1.10			Very small amount of polymerization				
Diisopropyl ether	1.0	1.44	1.87	1.79	1.38	0.51	1.09	2.6	2.1
"	3.0	1.07	1.88	1.77	1.36	0.61	0.92	3.8	1.9
"	4.5	1.54	1.86	1.64	7.01	7.01	4.86	8.7	3.8
"	6.0	0.95	1.88	1.69	3.29	3.00	2.78	6.4	3.5
"	9.0	1.00	1.87	1.66	3.34	3.12	7.31	2.6	7.8
"	12.0	0.98	1.87	1.65	2.92	2.92	5.45	3.3	5.6
"	6.0	0.34	1.90	1.73	1.66	1.27	2.74	2.7	4.08
"	6.0	1.46	1.86	1.65	3.92	3.92	4.34	4.6	2.27
"	6.0	0.55	1.89	1.65	2.56	1.94	3.92	3.1	3.86
"	6.0	1.74	1.85	1.62	8.15	8.15	15.2	3.2	3.98
"	6.0	1.97	1.84	1.63	11.7	11.7	15.1	4.8	5.05
"	6.0	1.22	0.94	0.83	2.81	2.81	2.78	12.1	3.85
"	6.0	1.06	2.82	2.63	5.26	4.96	—	—	2.77
Methylal	2.0	1.69			No polymerization				
Triethylamine	0.1	2.01	1.85	1.72	1.88	0.84	6.73	0.73	0.79
"	0.5	1.30	1.83	1.73	1.14	0.43	0.66	3.7	0.75
"	6.0	2.35			No polymerization				
Di-*n*-butyl sulfide	0.2	1.19	1.88	1.77	0.98	0.49	0.55	5.0	0.69
"	1.0	1.40	1.88	1.69	1.75	1.15	1.41	4.8	1.04
"	6.0	1.56			No polymerization				
Diallyl sulfide	6.0	2.06			No polymerization				
Thiophene	1.0	1.61	1.87	1.71	1.34	0.94	0.56	9.7	0.70
Triphenyl phosphine	2.0	1.73	1.86	1.86	0.74	0.74	—	—	0.36

TABLE III
Molecular Weight Data for Polymers

Initial polymer		Recrystallized polymer	
$M_T \times 10^{-3}$	$M_n \times 10^{-3}$	$M_T \times 10^{-3}$	$M_n \times 10^{-3}$
13.7	322	—	—
3.3	397	—	—
44	85	—	—
27	125	—	—
47	—	147	103
28	—	65	181
77	—	108	123

values were obtained by osmometry. Figures 8, 9, and 11 show the dependence of rate of polymerization on monomer concentration, catalyst concentration, and catalyst composition, respectively. In Table IV are given the results with supported catalysts, while in Table V the catalyst efficiencies are given. Table VI gives the data on a soluble cobalt system for butadiene.

The concentration of polymer–metal bonds (in mole $l.^{-1}$) is given by $N = KAG/A'$ where A and A' are the specific activities of the polymer and the methanol in the indicated units, G the polymer concentration (g. $l.^{-1}$) at the end of the reaction, and K the isotope effect.[1] Values for K in the literature for the methanol–$TiCl_3$–$AlEt_3$ catalyst are 3.7 for ethylene[1] and 1.3 and 1.0 for propylene.[2,3] The first of these values was taken in this work, since according to the theory of absolute reaction rates[3] K should lie between 1.76 and 10. An apparent rate constant (k_p) for propagation was calculated from N_f and the overall rate of polymerization at termination $R_f = k_p[M_f]N_f$. The relationship $k_p' = R_m/[VCl_3][M_0]$, where R_m is the maximum rate and $[M_0]$ is the initial monomer concentration, which relates to the amount of VCl_3 present rather than to the number of metal–polymer bonds, has also been calculated.

DISCUSSION

VCl_3–$AlEt_3$-Isoprene System

Typical time–conversion curves are shown in Figure 4. Following addition of the monomer the catalyst particles, which are initially of 30–50 μ size and evenly distributed, are rapidly coated with polymer and aggregate to a few large clusters. As reaction proceeds, these aggregates imbibe monomer and solvent until the characteristic purple color is present throughout the whole system. After a period in which the polymerization rate remains reasonably constant there is a fall-off in rate which is not entirely due to depletion of monomer. This behavior is characteristic of all the reactions, whether stirred or unstirred, but the magnitude of the acceleration period and the onset of the reduction in rate are very dependent

TABLE IV
Polymerization of Isoprene with Supported VCl_3 Catalysts

$AlEt_3/VCl_3/Ti(OEt)_4$ molar ratio	$[VCl_3]$, g. $l.^{-1}$	Monomer concentration, mole $l.^{-1}$		Polymerization rates, mole $l.^{-1}$ $sec.^{-1}$ $\times 10^5$		$N \times 10^4$, mole $l.^{-1}$	$R_f/N_f[M_f] \times 10^3$, l. $mole^{-1}$ $sec.^{-1}$	$R_m/[VCl_3][M_0] \times 10^3$, l. $mole^{-1}$ $sec.^{-1}$
		$[M_0]$	$[M_f]$	R_m	R_f			
10/1/0	0.25	1.85	1.84	0.137	0.137	0.114	6.7	0.47
10/1/0.5	0.13	1.92	1.80	0.78	0.78	0.590	7.3	4.91

TABLE V
Catalyst Efficiencies

System	$R_f/N_f[M_f]$ $\times 10^3$, l. mole^{-1} sec.$^{-1}$	$R_m/[VCl_3][M_0]$ $\times 10^3$, l. mole^{-1} sec.$^{-1}$	$\frac{[VCl_3]}{N}$
$AlEt_3/VCl_3$ 2/1	9.2 ± 5.6	0.67 ± 0.17	159
$AlEt_3/VCl_3/i\text{-}Pr_2O$ variable ratios	4.3 ± 2.2	3.71 ± 0.67	10–20
VCl_3 supported on TiO_2;	7.0 ± 0.3	0.47	142
on TiO_2 with $Ti(OEt)_4$		4.9	14
$AlEt_3/VCl_3/n\text{-}Bu_2S$ 2/1/variable	4.9 ± 0.1	0.87 ± 0.18	85

on the conditions of stirring. In fact with highly sheared solutions the acceleration period can almost be eliminated. Changes in the state of

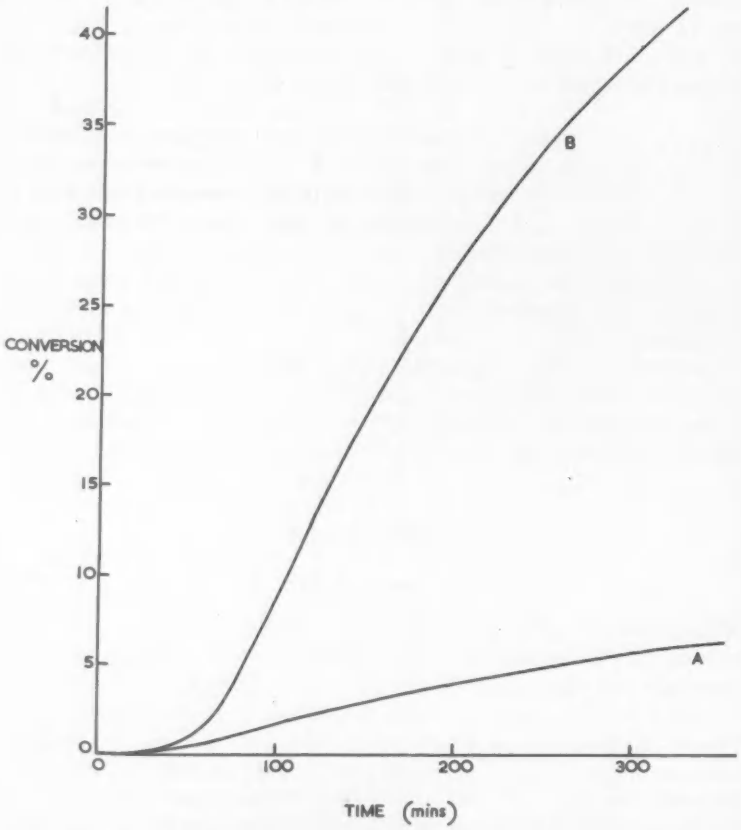


Fig. 4. Polymerization of isoprene ([M_0] = 1.86 mole l.$^{-1}$): (*A*) $AlEt_3/VCl_3$ = 2:1, [VCl_3] = 0.801 g. l.$^{-1}$; (*B*) $AlEt_3/VCl_3/i\text{-}Pr_2O$ = 2/1/6, [VCl_3] = 1.84 g. l.$^{-1}$.

TABLE VI
Polymerization of Butadiene with the Cobalt Naphthenate–Diethyl Aluminum Chloride–H_2O System[a]

Catalyst concentration, mole l.$^{-1}$	Monomer concentration, mole l.$^{-1}$		Average polymerization rate, R, mole l.$^{-1}$ sec.$^{-1}$	N_f, mole l.$^{-1}$	R / $N_f[M_f]$
	$[M_0]$	$[M_f]$			
2.8×10^{-5}	2.26	1.29	1.75×10^{-4}	8.0×10^{-5}	1.70

[a] $Co/Al/H_2O = 1/1000/100$; temperature = 25°C.; solvent = benzene.

aggregation of $TiCl_3$ in the polymerization of propylene have been reported by Natta.[9,10]

As shown by analysis of the supernatants this system is completely heterogeneous and no soluble catalytic species are formed. The propagation reaction is anionic and therefore the number of molecules linked to metal can be determined by terminating the reaction with tritiated alcohol and assaying the activity of the isolated polymer.

Kinetics. The acceleration periods in all cases showed a linear relationship between $\log \{(R_m - R_t)/(R_m - R_0)\}$ and P_t (Fig. 5), R_0 and R_t are the polymerization rates initially and at time t, and P_t, the yield of polymer

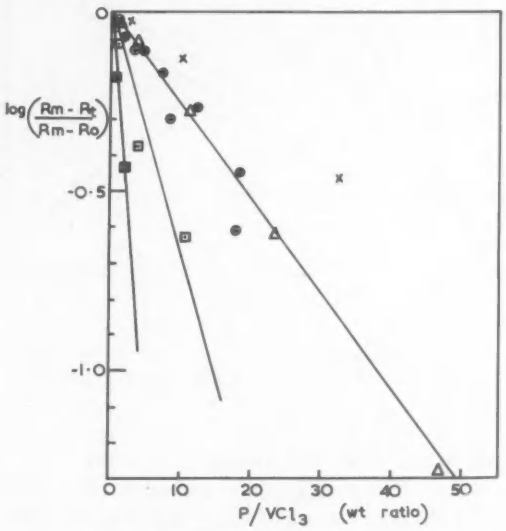


Fig. 5. Acceleration period in isoprene polymerization $[M_0] = 1.86$ mole l.$^{-1}$): (⊡) $AlEt_3/VCl_3 = 2/1$, $[VCl_3] = 0.806$ g. l.$^{-1}$; (⊠) $AlEt_3/VCl_3 = 2/1$, $[VCl_3] = 2.18$ g. l.$^{-1}$; (●) $AlEt_3/VCl_3/i\text{-}Pr_2O = 2/1/6$; $[VCl_3] = 1.71$ g. l.$^{-1}$; (⊕) $AlEt_3/VCl_3/i\text{-}Pr_2O = 2/1/6$; $[VCl_3] = 2.16$ g. l.$^{-1}$; (×) $AlEt_3/VCl_3/i\text{-}Pr_2O = 2/1/6$, $[VCl_3] = 0.336$ g. l.$^{-1}$ (△) $AlEt_3/VCl_3/i\text{-}Pr_2O = 2/1/6$, $[VCl_3] = 1.20$ g. l.$^{-1}$.

at time t. When expressed in terms of yield of polymer per gram of vanadium trichloride the data lie, within experimental error on the same line. This is in excellent agreement with the view that the initial acceleration results from the disruption, to a limiting size, of the heterogeneous crystal aggregates, by the growth of polymer molecules on the surface. Clearly according to this view it is changes in the catalyst brought about by polymer formation rather than a simple ageing process that results in the observed rates. Since the change in monomer concentration over the acceleration period is small R_m and R_t are approximately proportional to the corresponding changes in active centers N_m^* and N_t^*. It follows that the kinetic law governing the formation of new active centers has the form $dN^*/dP = k(N_m^* - N^*)$. From this relationship and noting that $dP/dt \simeq K'N^*$, it is readily shown that $R_t/R_m - R_t = Be^{Dt}$, where B and D are constants; $B = N_0^*/N_m^* - N_0^*$ and $D = kK'N_m^*$. Data plotted according to this relationship give reasonably good straight lines (Fig. 6). By contrast the equation log $\{R_m - R_t/R_m\}$ versus t developed by Keii[11] for the acceleration period for propylene when applied to these data (shown in Fig. 6 by the broken line) is not linear and therefore does not hold for this system.

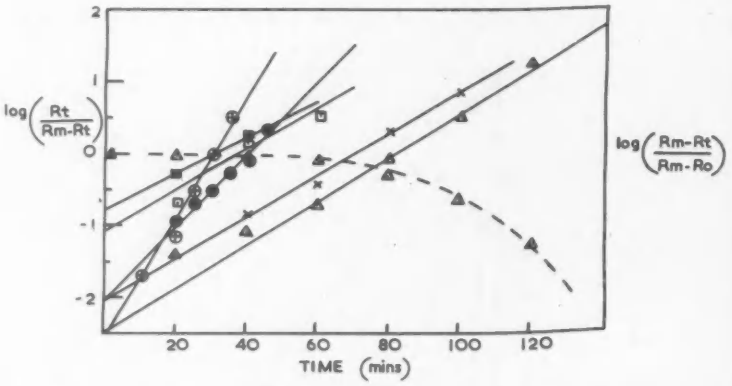


Fig. 6. Acceleration period in isoprene polymerization: (——) log $R_t/R_m - R_t$; (– –) log $(R_m - R_t/R_m - R_0)$. Symbols as in Figure 5.

The reactions all show a maximum in rate (Fig. 7), where the polymerization rate is first order with respect to monomer concentration (Fig. 8) and to VCl_3 concentration (Fig. 9). In Figure 10 is shown the change in concentration of metal–polymer bonds with time and the corresponding time–conversion curve for calculation of the number of active centers.

In the steady-rate region the number of metal–polymer bonds increases, and even at as low a conversion as 20% about 75% of the metal–polymer bonds are inactive. This can only be explained if it is assumed that some of them are not propagating chains. In terms of the mechanistic proposals

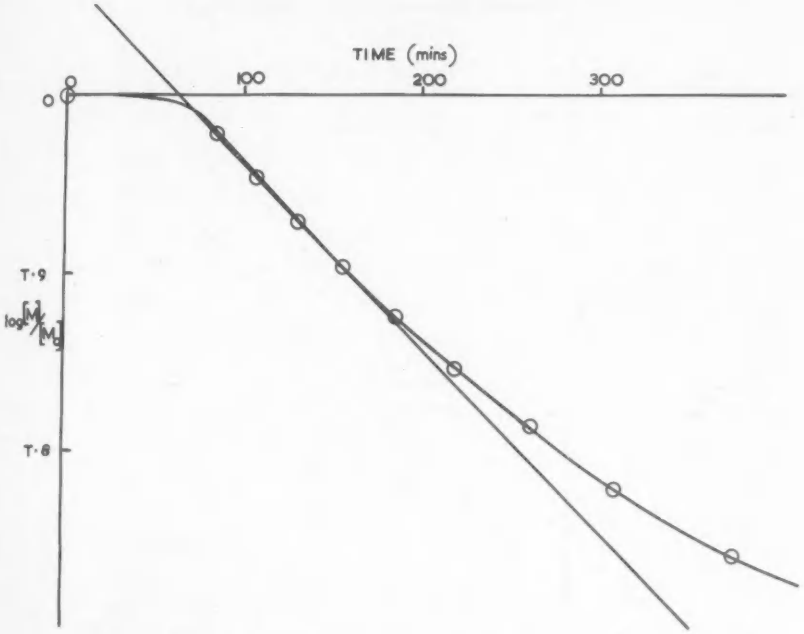


Fig. 7. Log [M]/[Mo] vs. time; [VCl_3] = 1.84 g. $l.^{-1}$, Al/V/*i*-Pr_2O = 2/1/6, [M_0] = 1.86 mole $l.^{-1}$.

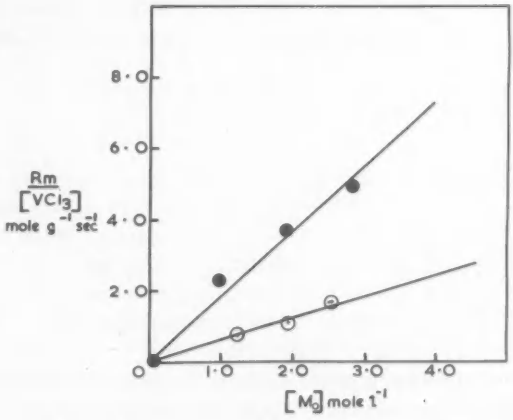


Fig. 8. Dependence of rate on monomer concentration: (○) Al/V = 2/1; (●) Al/V/*i*-Pr_2O = 2/1/6.

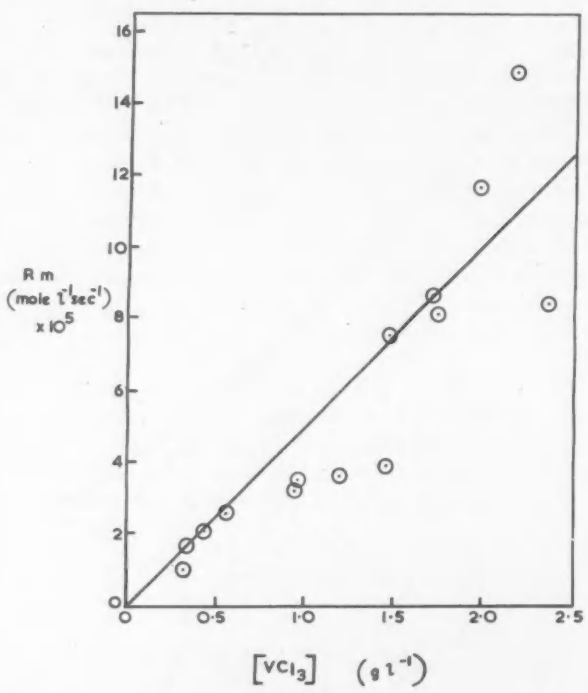
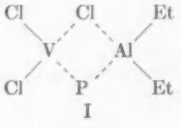
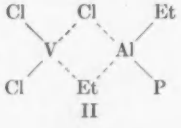


Fig. 9. Dependence of rate on VCl_3 concentration; Al/V/*i*-Pr_2O = 2/1/6, [M_0] = 1.86 mole $l.^{-1}$.

which have been made[12–14] the growing chains can be represented by structures of the type I, whereas the nongrowing polymer molecules would be of the types II or III produced by internal or external alkyl transfer reactions.



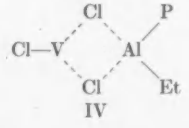
I



II

$Al(Et)_2P$

III



IV

The fact that little free polymer appears to be in the solvent above the catalyst suggests that most of the polymer is associated with the catalyst aggregate although in view of the gel-like structures which can be formed in polyisoprene solutions by $AlEt_3$ this inference is unreliable. It is also pos-

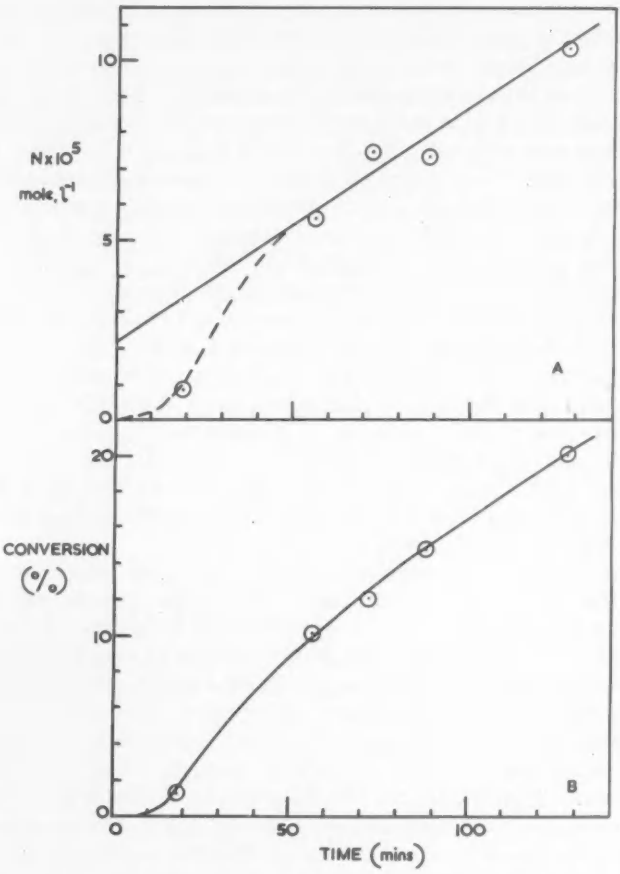


Fig. 10. Dependence of polymer–metal bonds on conversion; Al/V/*i*-Pr_2O = 2/1/6, $[M_0]$ = 3.09 mole $l.^{-1}$, $[VCl_3]$ = 1.57 g. $l.^{-1}$.

sible that a nongrowing site could be produced by reduction of the vanadium catalyst by loss of an alkyl radical (IV).*

From the initial concentration of active centers in Figure 10 (2.1×10^{-5} mole $l.^{-1}$) the rates of polymerization and the monomer concentrations the true rate constant for propagation is calculated to be 1.40 mole $l.^{-1}$ $sec.^{-1}$. This is very much larger than the apparent values given in Table V, showing that only a very small fraction of the polymer chains are active at any time during the reaction. During the acceleration period and at the

* Under the conditions of catalyst preparation about 2.5% of V^{2+} has been found by potentiometric titration. Whether this is associated with the active growing centers is not known.

maximum rate the concentration of active centers as a fraction of the total VCl_3 content is very small, as shown by the relative values of k_p and k_p' in the tables. There is however no evidence of termination by free radical decomposition of the polymer–catalyst complex or of hydride ion transfer or monomer transfer, since all the polymers molecules appear to possess radioactive endgroups after isolation (Table III). It is clear that a substantial number of low molecular weight polymers are formed since the number-average molecular weights calculated from the number of metal–polymer bonds are much lower than the osmotic molecular weights where loss of low polymer occurs through the membrane. Recrystallization of polymer to remove the low molecular weight species results in better agreement between molecular weights from osmotic and activity measurements.

Although the tabulated velocity constants k_p and k_p' do not represent the actual rates of growth from an active site if, at comparable conversions, it is assumed that the fraction of active centers in the total of metal–polymer bonds is approximately the same, it is apparent that the propagation reaction is not greatly influenced by the experimental conditions. Thus variation of Al/V ratio, addition of electron donors, presence of VCl_3 as crystallites, or as a deposit on an inert support such as TiO_2 (Table IV) do not alter the magnitudes of k_p and k_p'.

No attempt has been made to analyze the kinetics at higher conversions where the reaction rate begins to fall. It is presumed, as has been demonstrated in other systems, that at the later stages the reaction is controlled by diffusion of monomer into the gel-like polymer or since polyisoprene itself contains double bonds, that the polymer is competing with the monomer for adsorption at the VCl_3 surface.*

Influence of Electron Donors. The effect of electron donors on Ziegler-Natta catalyst systems has been widely studied. Thus with propylene the influence of ethers, amines, and thioethers have been examined by several investigators,[15–18] and there are numerous examples in the patent literature of the course of these and other reactions being modified by addition of electron donors.[19] With $TiCl_3$ strong complexes were thought to be formed between the transition metal compound and the electron donor to produce catalyst centers of greater activity; the ability of the electron donor to coordinate with the surface was presumed to depend on its structure and on steric factors.

In the present system the activities of the electron donors have been found to be quite different. Unlike propylene polymerizations, the effect of amines is to inhibit the polymerization of isoprene, and we attribute this to competition between monomer and amine for the surface of the catalyst particle. With less powerful electron donors, such as aliphatic ethers or thioethers, the rate is not reduced and may in some cases be increased, as with the other systems. Triethylamine at low concentrations has little effect on the reaction but at amine/V ratios above 0.5 the reaction stops.

* There is some evidence to show that carbon–carbon crosslinks are formed at the higher conversions, presumably by growth from the small proportion of 3,4 addition.

Dibutyl sulfide increases the rate at $Bu_2S/V = 1$ but stops the reactions at $Bu_2S/V = 6$. Ethers also inhibit the reaction at high ratios of ether/V. These rates relate to a particular ratio of $Al/V = 2$, but if this ratio is increased then a greater proportion of electron donor can be tolerated (Table IV, Fig. 11). This further supports the view that there is competition for the electron donor between the aluminum alkyl and the transition metal halide. The results of the various systems are given in Tables IV and V. As discussed above and in contrast with Boor's[20] findings with propylene, we find the propagation velocity not to be influenced by the addition of electron donors. Changes in rate, therefore, must be attributed to either an increase or decrease in the number of active centers. The intercept of

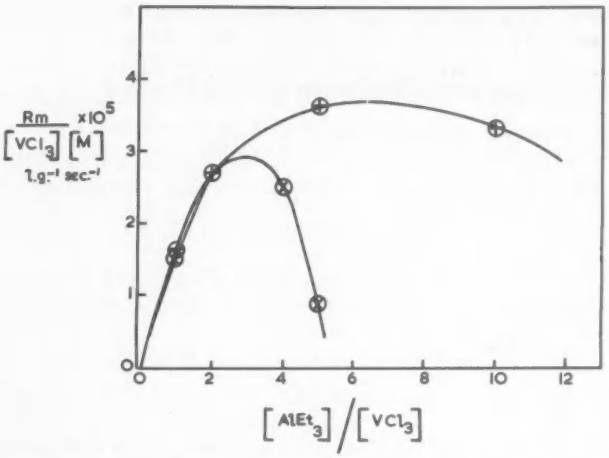


Fig. 11. Effect of $AlEt_3/VCl_3/i\text{-}Pr_2O$ ratios on polymerization rates: (⊗) $VCl_3/i\text{-}Pr_2O$ = 1/6; (⊕) $AlEt_3/i\text{-}Pr_2O$ = 1/3.

$\log (R_t/R_m - R_t)$ versus t is a measure of the change in the number of active sites during the acceleration period. Using this relationship it is found that in the unmodified $VCl_3/AlEt_3$ system there is a tenfold increase in the number of centers, whereas in the presence of an electron donor the number of centers increases one hundredfold.

Catalyst Efficiency. From the number of metal–polymer bonds and the weight of VCl_3 it is possible to estimate the maximum number of vanadium atoms which have participated in the polymerization. These are shown in Table V. In view of the transfer reactions which have been shown to occur the numbers of vanadium atoms which are considerd active are much too large but the relative values can be used. The results show a wide variation between the different systems indicating marked changes in the activity of the catalyst surface. However, many of the polymer molecules, as has been indicated above, are of very low molecular weight—and

may, in fact, be produced by a separate mechanism. The number of active centers producing high molecular weight polymer is much smaller (on average by a factor of 10). Thus we would conclude that only one vanadium atom in several hundred results in the formation of high molecular weight polymer.

Co (Naphthenate)–$AlEt_2Cl$–H_2O–Butadiene System

To compare with the heterogeneous system in which only a very small proportion of active sites are produced it was thought desirable to examine a soluble catalyst. Preliminary data (Table VI) on a soluble cobalt system show, as would be expected, that every transition metal atom is present in an active center. The function of the water in the polymerization is not obvious, but it does not apparently change the anionic character of the reaction.

Influence of Additives on Polymer Structure

It might be expected that the addition of electron donors would alter the structure of the polymer. However, in all cases in which polymer was produced electron donors had no effect on structure so far as could be ascer-

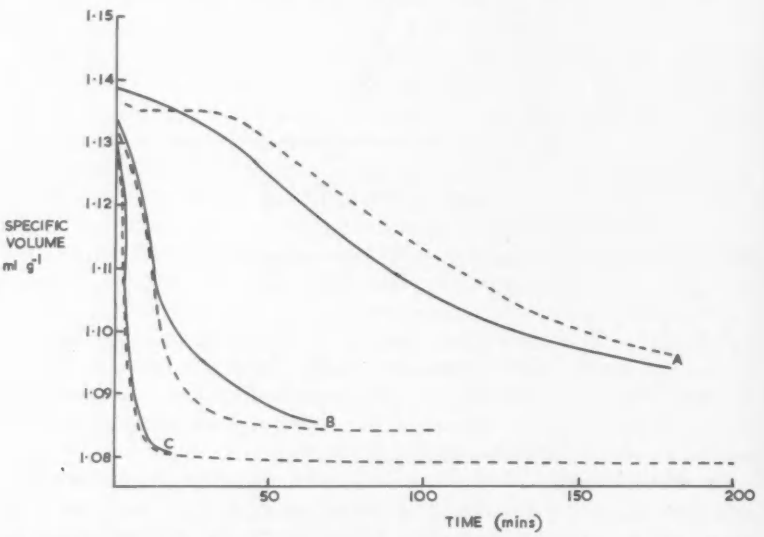


Fig. 12. Crystallization rate curves (——) for $AlEt_3$–VCl_3 system and (- -) $AlEt_3$/VCl_3/*i*-Pr_2O system at various crystallization temperatures: (*A*) 50°C.; (*B*) 40°C.; (*C*) 30°C.

tained. The infrared spectra were identical, and rates and percentages of crystallization were in the same range (Fig. 12). Electron donors are known to have a marked influence on many ionic diene polymerizations.

The effect of ethers on the polymerization of isoprene or butadiene by lithium alkyls is well known, and recently it has been shown that ethers or amines change the structure of polymers of hexa-1,5-diene prepared with vanadium halide–aluminium alkyls from ca. 90% cyclic structure to ca. 70% 1,2 addition.[21] In these instances it seems likely that the ether blocks one or more of the coordination sites on the transition metal halide and permits adsorption at only one double bond of the monomer.

In the isoprene–VCl_3–$AlEt_3$ system electron donors apparently liberate a greater surface area on which reaction can proceed. They do not seem to influence the way the monomer is absorbed or the rate of addition, unless they are such powerful donors or are present in high concentrations such that they preferentially coordinate with metal alkyl and/or metal halide to the exclusion of the monomer and/or metal alkyl. They may increase the effective active area of catalyst either by assisting in the break-up of transition metal halide aggregates by penetration of the crystal lattice, or by a solvation effect, preventing aggregation of the catalyst surfaces.

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Synopsis

The heterogeneous polymerization of isoprene with the use of vanadium trichloride and triethyl aluminum as catalyst is characterized by a slow initial reaction followed by a period of acceleration to a steady rate. The kinetics of this acceleration period are consistent with the view that crystals or crystal aggregates of the vanadium trichloride are broken down by the growing polymer chains. The number of carbon–metal bonds, measured by terminating the reaction with tritiated methanol and assaying the polymer, increases throughout the polymerization. From the change in number of carbon–metal bonds with conversion over the steady polymerization range it is deduced that alkyl transfer reactions are of frequent occurrence but, since all the polymer molecules contain tritium, monomer or hydride transfer reactions do not occur. Electron donors influence the reaction by increasing the number of reactive centers from which polymerization can occur but do not alter the growth reaction. They do not result in the formation of soluble species, nor do they change the structure of the polymer produced. The reaction rate passes through a maximum as the concentration of electron donor is increased, presumably as a result of competition between monomer and electron donor for the surface of the transition metal halide, and strong donors such as tertiary amines inhibit the reaction at low concentrations. From the molecular weights of the polymers and the number of active centers it is estimated that not more than 1 in 160 of the vanadium atoms in the unmodified catalyst participate in the polymerization. The polymer is of high molecular weight but there is also formed a low molecular weight fraction which comprises a large fraction of the total number of polymer molecules formed. By contrast with this system, the soluble cobalt system is used for the polymerization of butadiene, where each transition metal atom produces on average about three polymer molecules.

Résumé

La polymérisation hétérogène de l'isoprène catalysée par le trichlorure de vanadium et le triéthylaluminium se caractérise par une vitesse de réaction initiale lente suivie d'une période d'accélération menant à une vitesse stationnaire. La cinétique de cette période d'accélération est en accord avec le concept d'une rupture des cristaux ou des agrégats cristallins par les chaînes polymériques en croissance. Le nombre de liens carbone-métal, mesuré en effectuant la terminaison de la réaction au moyen de méthanol titré et en dosant la radioactivité du polymère, augmente au cours de la polymérisation. De cette variation du nombre de liens carbone-métal en fonction de la conversion du monomère dans le domaine de stationnarité de la vitesse de polymérisation, on déduit que les réactions de transfert d'alcoyle se produisent fréquemment mais puisque les molécules de polymère contiennent du tritium, les réactions de transfert sur monomère et de transfert d'hydrure ne se produisent pas. Les conneurs d'électron influencent al réaction en augmentant le nombre de centres réactionnels d'où la polymérisation peut être initiée mais n'affectent pas la réaction de propagation. Ils ne provoquent pas la formation d'espèce soluble et ne causent pas de variation de structure du polymère formé. La vitesse de réaction passe par un maximum lorsqu'on augmente la concentration en donneur d'électron, probablement à la suite d'une compétition entre le monomère et le donneur d'électron vis-à-vis de la surface de l'halogénure du métal de transition et de forts donneurs d'électron tels que les amines tertiaires inhibent la réaction à basse concentration. Connaissant le poids moléculaire des polymères et le nombre de centres actifs, on estime qu'il n'y a pas plus de $1/160^{\text{è}}$ des atomes de vanadium du catalyseur non-modifié qui participe à la polymérisation. Le polymère possède un poids moléculaire élevé mais il se forme aussi des fractions de bas poids moléculaire qui constituent une grande partie du nombre total de molécules de polymère formées. Contrairement au système ci-dessus, dans le système soluble au cobalt utilisé pour la polymérisation du butadiène, chaque atome du métal de transition produit en moyenne trois molécules de polymère.

Zusammenfassung

Für die heterogene Polymerisation von Isopren mit Vanadiumtrichlorid und Aluminiumtriäthyl als Katalysator ist eine langsame Anfangsreaktion, gefolgt von einer Periode der Beschleunigung bis zu einem stationären Zustand charakteristisch. Die Kinetik dieser Beschleunigungsperiode steht mit der Vorstellung im Einklang, dass die Vanadiumtrichloridkristalle oder -kristallaggregate durch die wachsenden Ketten zerstört werden. Die durch Abbruch der Reaktion mit tritiummarkiertem Methanol und Untersuchung des Polymeren bestimmte Anzahl von Kohlenstoff-Metall-Bindungen nimmt im Laufe der Polymerisation zu. Aus der Änderung der Anzahl von Kohlenstoff-Metall-Bindungen mit dem Umsatz in einem Bereich stationärer Polymerisation wird geschlossen, dass zwar haufig Äthylübertragung, nicht aber Monomer- oder Hydridübertragung auftritt, da alle Polymermolekule Tritium enthalten. Elektronendonoren erhöhen zwar die Zahl der reaktiven Zentren, an denen die Polymerisation stattffinden kann, beeinflussen aber die Wachstumsreaktion nicht. Sie führen weder zur Bildung einer löslichen Substanz noch verändern sie die Struktur des gebildeten Polymeren. Die Reaktionsgeschwindigkeit geht bei zunehmender Elektronendonor-Konzentration durch ein Maximum, wahrscheinlich infolge der Kompetition zwischen Monomerem und Elektronendonor an der Oberfläche des Übergangsmetall-Halogenides. Starke Donoren wie etwa tertiäre Amine inhibieren bei niedriger Konzentration die Reaktion. Aus dem Molekulargewicht der Polymeren und der Zahl der aktiven Zentren wurde berechnet, dass nur eines von 160 Vanadiumatomen des unmodifizierten Katalysators an der Polymerisation teilnimmt. Das Polymere hat zwar ein hohes Molekulargewicht, doch wird auch eine niedrigmolekulare Fraktion begildet, die einen grossen Teil der Gesamtzahl der gebildeten Polymermoleküle ausmacht. Im Gegensatz zu diesem System steht das bei der Polymerisation von Butadien verwendete lösliche Kobaltsystem, bei welchem jedes Übergangsmetallatom zur Bildung von durchschnittlich etwa drei Polymermolekülen fuhrt.

Discussion

A. D. Caunt (*I.C.I. Ltd., Herts, Great Britain*): May I raise two questions: Firstly, concerning the derivation of the number of active centers by the extrapolation of the number of polymer molecules against time (Fig. 10 upper graph). In cases where induction periods are found, such as the present one, such an extrapolation is not logically sound. We have cases where induction periods of an hour are experienced in propylene polymerization, and such extrapolations would give the absurd result of negative number of centers. It is much sounder to plot number of polymer molecules against conversion as a measure of polymerization as we have employed in our own paper. From rough calculations of the data presented in Dr. Vaughan's graphs in Figure 10 it appears that by chance the figure deduced by Dr. Vaughan is not much altered by adopting the procedure proposed, but in other cases there are possibly serious deviations.

Secondly, concerning the effects of donor compounds which in Dr. Vaughan's experiments increased the rate without serious effects on stereospecificity. We can site similar cases with propylene polymerization where these compounds are acting by complexing with an inhibitor produced as a by-product of the reaction of alkyl and catalyst during polymerization. The systems described by Dr. Coover using hexamethylphosphoramide are in principal the same as our own. Could this also be the case with Dr. Coover's system?

G. Vaughan: In our systems experiments which show longer induction periods than corresponding charges in the numbers of C—Al bonds so that extrapolations still give positive values for the number of active centers. Since we have shown that all the polymer molecules are labelled we feel that the technique used is sound and not purely fortuitous. We have indicated in the paper that there are certain approximations made already so we are not claiming our propagation constants as very absolute. In

fanswer to the second part. We take great care to remove the impurities from our starting materials so the possibility of the donor acting in this way is remote. There is the chance that certain retarders are generated in the system as indicated by Dr. Caunt, but as our measurements are made at low conversions the concentration of these compared with aluminium trialkyl will be very low. In addition it is sufficient to explain the large increases in the number of active sites in these systems by such a mechanism. At this stage, as indicated in the paper we, do not know how the donor functions is causing the larger increases in rate reported in several papers.

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Polymerization of Butadiene by Triisobutylaluminum Diisopropyl Etherate and Titanium Tetraiodide

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INTRODUCTION

The discovery by Ziegler of coordination anionic catalysts has stimulated much research which has led to the synthesis of a large number of new polymer molecules.[1] By employing these initiators to polymerize butadiene for example, it has now become possible through appropriate choice of the catalyst to prepare four types of stereoregular polymer, namely 1,4-*cis*, 1,4-*trans*, and vinyl, the latter having either isotactic or syndiotactic structures (Table I).

Little is yet known about the steps occurring during chain growth which give rise to stereoregular polymers. To prepare stereoregular polymers from α-olefins such as propylene and butene-1, it appears that the catalyst must be heterogeneous. Experiments have been made to correlate the microstructure of the polymer with the ionic diameter of the metal of the organometallic catalyst component and the crystal structure of the transition metal halide.[9–11] Monomers such as diolefins and vinyl ethers, which have two electron-rich groups, can be polymerized to stereoregular polymers by soluble catalysts.[9]

Another subject of interest about which little information is yet available is the kinetics of Ziegler polymerizations. Because the active ends of grow-

TABLE I
Stereospecificity of Butadiene Polymerizations in Hydrocarbon Solvents

Catalyst	Microstructure	Reference
$Al(C_2H_5)_3/TiI_4$	92% *cis*	2
$Al(C_2H_5)_3/TiI_4/(iso\ C_2H_7)_2O$	92–94% *cis*	3
$Al(C_2H_5)_2Cl/Co(acetylacetonate)_2$	96–98% *cis*	4
$Al(C_2H_5)_3/VCl_4$	98% *trans*	5
$Al(C_2H_5)_3/VCl_3$	98% *trans*	6
$Al(C_2H_5)_3/VOCl_2$	98% *trans*	5
$Al(C_2H_5)_3/V(acetylacetonate)_3$	95% vinyl (syndiotactic)	7
$Al(C_2H_5)_3/Cr(acetylacetonate)_3$, (Al/Cr) = 2	90% vinyl (syndiotactic)	8
$Al(C_2H_5)_3/Cr(acetylacetonate)_3$, (Al/Cr) = 10	90% vinyl (isotactic)	8

ing polymer molecules appear to be associated with the catalyst, many variations in behavior have been observed when different catalysts have been used which makes generalizations difficult. For example, both the mechanisms and rates of the termination reactions that occur during the polymerizations of ethylene and of propylene are dependent on the catalyst, and no explanation is available that accounts for this.[10–17]

In this investigation, the kinetics of the polymerization of butadiene by a catalyst consisting of triisobutylaluminum, diisopropyl ether, and titanium tetraiodide were studied with the objective of determining factors which influenced the rates of the chain propagating and termination reactions. The diisopropyl ether was present in these systems for the purpose of maintaining high *cis* contents in the polybutadienes.[3] The microstructures of many of the polymers were also measured, but no consideration was given to the chemical composition of the catalyst.

EXPERIMENTAL

The polymerizations were carried out under an atmosphere of nitrogen in either 7-oz. crown-capped bottles which were rotated end-over-end in a constant temperature bath or in a 2-liter glass reactor equipped with a stirrer and coils through which a thermostatted solution was pumped. When the latter technique was employed, the butadiene conversion and the intrinsic viscosity of the polymer in toluene at 30°C. were measured as functions of time by removing aliquots from the reaction system and recovering the polymer. In all instances, the reactions were started by adding titanium tetraiodide to butadiene and triisobutylaluminum diisopropyl etherate dissolved in heptane, which was used as solvent in virtually all the experiments, or benzene; unless otherwise mentioned, the molar ratio of triisobutylaluminum to ether was one. The *cis*, *trans*, and vinyl contents of the polymers were measured by determining the relative infrared absorptivities of polymer films at 737, 909, and 967 cm.$^{-1}$, and by assuming the unsaturation to be 100% of the theoretical. Some of the polymers were also fractionated by the method described by Hulme and McLeod.[18]

Triisobutylaluminum (supplied by Texas Alkyls) reported to be 90% minimum in triisobutylaluminum and 10% maximum in diisobutylaluminum hydride and anhydrous titanium tetraiodide (supplied by A. D. McKay, New York) were used without further purification. Phillips Pure Grade butadiene (> 99%) was dried just prior to use by being passed in liquid form through columns containing calcium hydride and Linde 4A molecular sieves. Phillips Pure Grade heptane (> 99%) was further purified by distillation from triisobutyl aluminum and was passed through a column of Linde 4A molecular sieves directly into the reaction vessel. Phillips Pure Grade benzene (> 99%) was dried by an azeotropic distillation in which the first fraction amounting to 10% and containing most of the water was discarded. The remainder was passed through a column of Linde 4A molecular sieves just before use.

RESULTS

When the catalyst components were mixed in the presence of butadiene and diluent, rapid changes in color were observed, and polymerization began almost immediately. The catalyst appeared to the naked eye to be soluble, and centrifuging of the polymerization system did not cause a solid material to settle out. The polymer itself is soluble in both heptane and benzene and remained in solution throughout the polymerization.

In heptane diluent at molar ratios of Al:Ti 2.8–25.9, the polymer yield increased very rapidly with time during the early stages of the polymerization, but the reaction almost ceased at butadiene conversions as low as 30–60% (Fig. 1). In this and most of the figures that follow, the points are

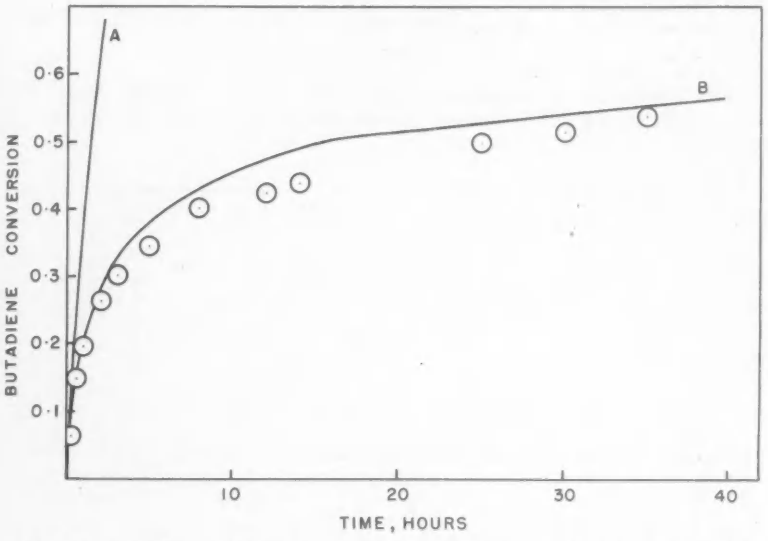

Fig. 1. The variation of butadiene conversion with time at 2°C. in heptane: (*A*) termination negligible; (*B*) calculated by eq. (4) for the conditions employed in experiment 1; (O) experiment 1.

experimental, and curves were calculated by equations that will be described later. At a given catalyst concentration and polymerization time, the butadiene conversion was independent of the initial concentration of butadiene (Table II) but Figure 2 shows that the polymer yield in a given time increased rapidly with catalyst concentration when it was low and then approached an almost constant value. At Al/Ti < 2.8 or Al/Ti > 25.9 very little polymerization was observed; the system was not investigated under these conditions.

Figure 3 shows that the intrinsic viscosity of the polymer increased with increasing butadiene conversion to an approximately asymptotic value.

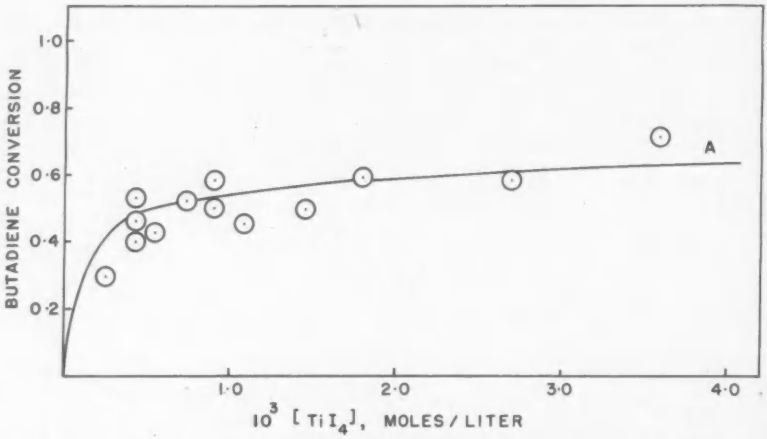

Fig. 2. The variation of butadiene conversion with titanium tetraiodide concentration at 24 hr. and 2°C. in heptane: (*A*) calculated by eq. (4) for Al/Ti = 5.55.

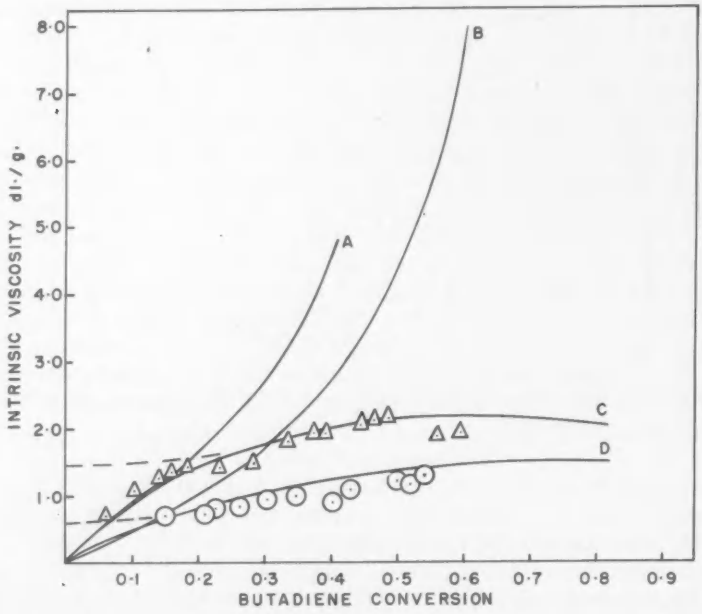

Fig. 3. The variation of intrinsic viscosity with butadiene conversion at 2°C. in heptane: (*A*) calculated by eq. (10) for conditions employed in experiment 1; (*B*) calculated by eq. (10) for conditions employed in experiment 3; (*C*) calculated by eq. (8) for conditions employed in experiment 1; (*D*) calculated by eq. (8) for the conditions employed in experiment 3; (○) experiments 1 and 2; (△) experiments 3 and 4.

TABLE II
Effect of Initial Butadiene Concentration on Polymer Yield in Heptane at 24 hr. and 2°C., $[TiI_4] = 1.08 \times 10^{-3}$ moles/l., Al/Ti = 5.55

$[M_0]$, moles/l.	Fractional butadiene conversion
0.910	0.345
1.14	0.437
1.37	0.473
1.82	0.417
2.05	0.482
2.85	0.477

For a given polymerization time, the intrinsic viscosity increased with increasing initial butadiene concentration and decreasing titanium tetraiodide concentration, respectively (Figs. 4 and 5).

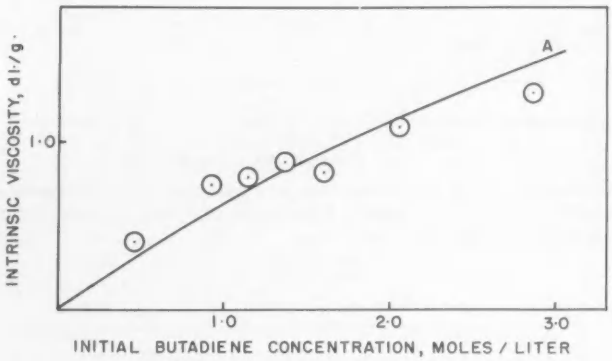

Fig. 4. The variation of intrinsic viscosity with the initial butadiene concentration at 24 hr. and 2°C. in heptane: (*A*) calculated by eqs. (4) and (8) for $[TiI_4] = 1.08 \times 10^{-3}$ moles/l. and Al/Ti = 5.55.

The integral molecular weight distributions of three polymers removed from reaction mixtures after 35 hr. polymerization were virtually identical (Fig. 6). Furthermore, they agree closely with the most probable distribution curve calculated by the equation

$$\sum \cdot w_j = [1 + (j/\bar{N}_n)]\exp\{j/\bar{N}_n\} \quad (1)$$

where j is the degree of polymerization of a fraction and $\bar{N}_n$ is the number-average degree of polymerization of the whole polymer.[19] The results in Figure 6 were plotted against the ratio, $[n]_f^{1/a}/[n]^{1/a}$, to minimize differences in molecular weight distributions arising from differences in whole polymer intrinsic viscosities, $[n]$. In toluene, a is assumed to be 0.77.[20]

Many of the polymers which were prepared were analyzed by infrared for *cis*, *trans*, and vinyl contents. Regardless of the experimental conditions, the per cent vinyl remained constant at 4.9 ± 0.9%. The *cis* content in-

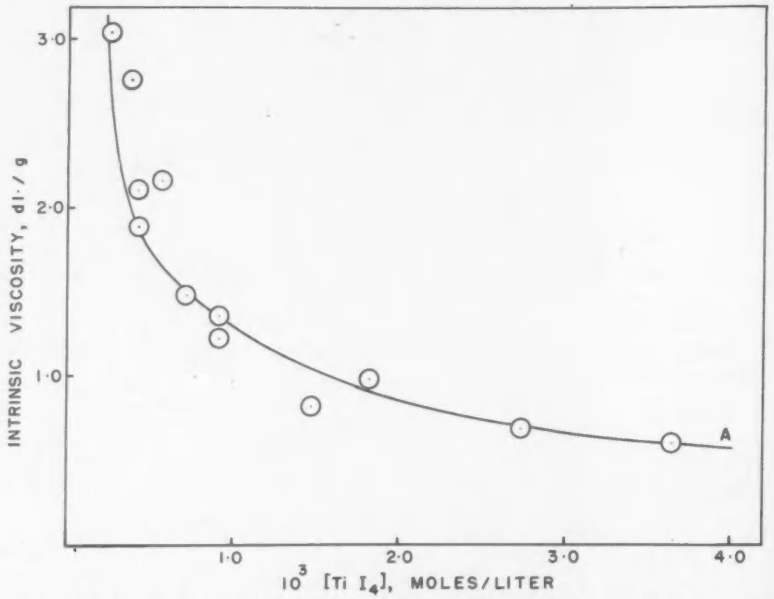

Fig. 5. The variation of the intrinsic viscosity with the titanium tetraiodide concentration at 24 hr. and 2°C. in heptane: (*A*) calculated by eqs. (4) and (8) for $[M_0]$ = 2.28 moles/l. and Al/Ti = 5.55.

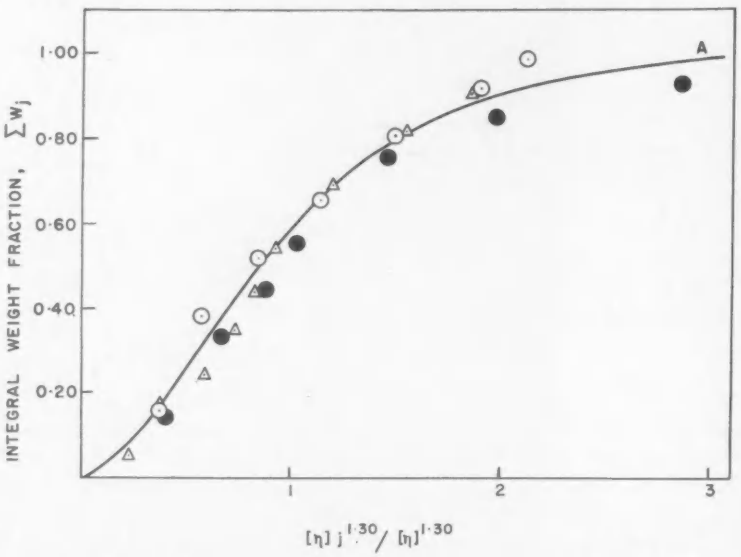

Fig. 6. The integral molecular weight distribution of *cis*-1,4-polybutadiene prepared in heptane at 2°C.: (*A*) calculated by eq. (1); (○) experiment 3, $[\eta]$ = 2.16; (●) experiment 4, $[\eta]$ = 1.92; (△) experiment 6, $[\eta]$ = 3.41.

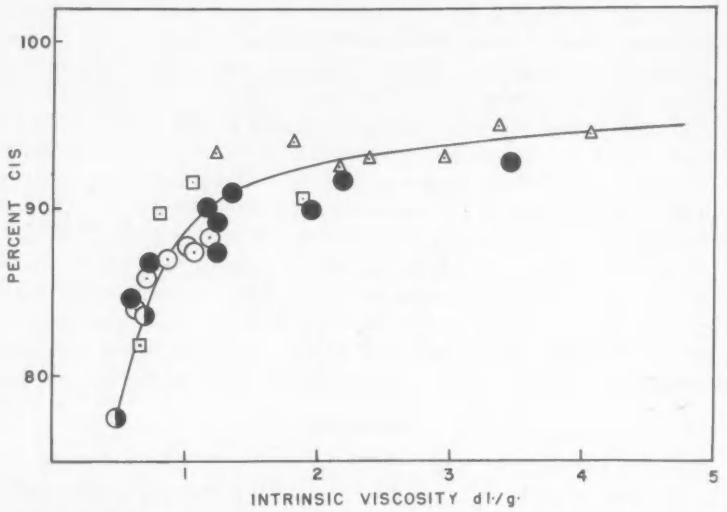

Fig. 7. The relation between the *cis* level and the intrinsic viscosity of the polybutadiene: (○) $[TiI_4] = 1.08 \times 10^{-3}$ moles/l., Al/Ti = 9.26, $0.455 < [M_0] < 3.42$ in heptane at 13°C. and 24 hr.; (△) $[TiI_4] = 0.72 \times 10^{-3}$ moles/l., Al/Ti = 25.0, $0.455 < [M_0] < 3.42$ in benzene at 13°C. and 24 hr.; (●) $[M_0] = 2.28$ moles/l. Al/Ti = 5.55, $0.24 \times 10^{-3} < [TiI_4] < 3.60 \times 10^{-3}$ in heptane at 2°C. and 24 hr.; (◑) $[M_0] = 0.569$ moles/l., Al/Ti = 5.55, $[TiI_4]$ 2 0.540 and 3.60×10^{-3} moles/l. in heptane at 2°C. and 24 hr.; (□) $[M_0] = 1.90$ moles/l., Al/Ti = 5.0, $1.20 \times 10^{-3} < [TiI_4] < 4.80 \times 10^{-3}$ in benzene at 13°C. and 5 hr.

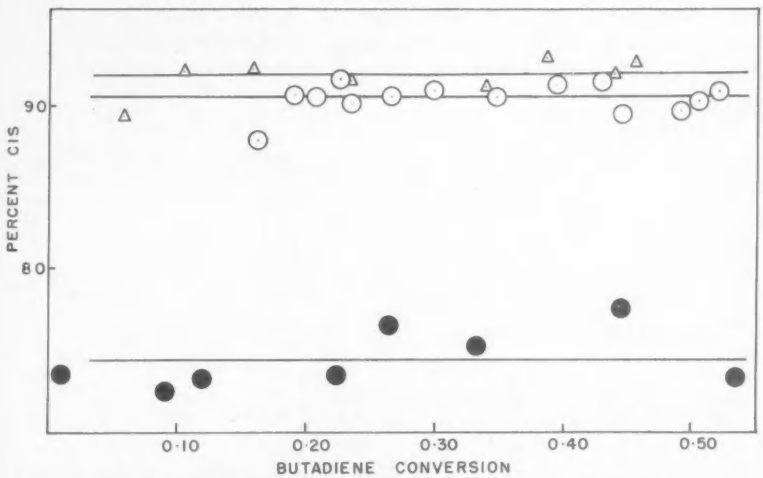

Fig. 8. The relation between the *cis* level of the polybutadiene and the butadiene conversion in heptane at 2°C.: (○) experiment 2; (△) experiment 7; (●) $[M_0] = 0.569$ moles/l., Al/Ti = 5.55, $[TiI_4] = 3.60 \times 10^{-3}$ moles/l.

creased with increasing initial butadiene concentration and decreasing titanium tetraiodide concentration but tended to be insensitive to the ratio of aluminum to titanium. Similar variations also caused the intrinsic viscosity to increase, and Figure 7 shows that the *cis* contents and the intrinsic viscosities of the polymers are correlated for the experimental conditions employed. Figure 8 shows that the *cis* contents were independent of butadiene conversion, suggesting that it was determined by the concentration of butadiene at the beginning of the polymerization. The polymers prepared in experiments 3, 4, 5, 7, 8, and 9 were 91.7, 89.9, 90.5, 91.2, 89.0, and 85.5% in *cis*, respectively, which indicates that the *cis* content tended to decrease slightly with increasing polymerization temperature. The fractionation of polymers of this type indicated that, except for the very low molecular weight fractions which were lower in *cis*, the microstructures of the fractions were independent of their molecular weights.[21]

Discussion

The observed decrease in polymerization rate with time was much more marked than calculated for a reaction first order in monomer concentration and in which the concentration of catalytic species was constant (curve *A* in Fig. 1). This was not due to the reaction order in butadiene being greater than one since the butadiene conversion was independent of the initial butadiene concentration. The fact that the polymer remained soluble in the polymerization mixture rules out the possibility of catalytic species becoming occluded in precipitated polymer and thus causing the reaction rate to decrease. This behavior is best explained by the following kinetic scheme provided the initiation is assumed to be either very rapid or very slow relative to all the other steps. If the rate of initiation had been equivalent to the rates of the other steps, the polymerization rate would have increased with time during the early stages of reaction and this was not observed.

Initiation:

$$\text{Al}(i\text{-C}_4\text{H}_9)_3 \text{ etherate} + \text{TiI}_4 \xrightarrow{\text{butadiene}} \text{X}$$

$$\text{X} + \text{X} \xrightarrow{k_i} 2\text{C}^*$$

Propagation:

$$\text{M}_r\text{C}^* + \text{M} \xrightarrow{k_p} \text{M}_{r+1}\text{C}^*$$

Termination:

$$\text{M}_r\text{C}^* + \text{M}_s\text{C}^* \xrightarrow{k_t} \text{M}_r + \text{M}_s + 2\text{C}$$

Transfer:

$$\text{M}_r\text{C}^* + \text{T} \xrightarrow{k_{tr}} \text{M}_r + \text{C}^* + \text{T}'$$

If the second step of the initiation was very slow relative to all the other reactions, the kinetics would be stationary and we obtain

$$\ln[\text{M}_0/\text{M}] = [k_p/(2k_tk_i)^{1/2} \ln (1 + k_i[\text{X}_0]t)] \qquad (2)$$

TABLE III
Relative Values of the Rate Constants in Heptane

Expt. No.	$[M_0]$, moles/l.	$10^3[TiI_4]$, moles/l.	$\frac{Al}{Ti}$	Temp., °C.	A	$B[TiI_4]$	$\frac{k_{tr}[T]}{Qk_p}$	$\frac{[Co^*]}{Q}$
1	2.28	0.90	5.55	2	0.157 ± 0.003	3.0	0.48 ± 0.1	0.59 ± 0.05
2	2.28	0.90	5.55	2	0.155 ± 0.002	3.5	0.67	0.54
3	2.28	0.42	5.55	2	0.153 ± 0.002	1.8	0.36 ± 0.02	0.20 ± 0.02
4	2.28	0.42	5.55	2	0.242 ± 0.01	1.2	0.46 ± 0.04	0.20 ± 0.01
5	1.14	0.42	5.55	2	0.204 ± 0.001	1.8	0.30 ± 0.02	0.08 ± 0.01
6	2.28	0.24	5.55	2	0.119 ± 0.03	0.70	0.33 ± 0.02	0.03 ± 0.004
7	2.28	0.42	5.55	13	0.255	2.0	0.27 ± 0.02	0.30 ± 0.02
8	1.14	0.42	5.55	14	0.367	1.0	0.30 ± 0.1	0.17 ± 0.02
9	1.14	0.42	5.55	25	0.412	1.0	0.23 ± 0.02	0.29 ± 0.02

On the other hand, if both initiation steps were very rapid relative to the other reactions, the kinetics would be nonstationary and[22]

$$1n[M_0]/[M] = (k_p/2k_t)1n(1 + 2k_t[C_0^*]t) \tag{3}$$

Hence, for both conditions at constant Al/Ti

$$1n[M_0]/[M] = A1n(1 + B[TiI_4]t) \tag{4}$$

Straight lines were observed when the results were plotted according to eq. (4), and by least mean square calculations values of B were chosen which caused these to extrapolate to the origin. The values of A and B shown in Table III were insensitive to the experimental conditions at 2°C. and Al/Ti = 5.55. The very small standard deviations of A show that the fit of the experimental results with eq. (4) was close and, therefore, that one of the two postulated kinetic schemes is appropriate. This is also demonstrated by the curves in Figures 1 and 2, that were calculated by eq. (4) for $A = 0.172$ and $B = 3670$.

Raising the temperature was without significant effect on B but caused A to increase according to the following relation

$$1 + \log A = 5.5 \pm 1.3 - (1.4 \pm 0.4/10^{-3}T) \tag{5}$$

From this, the difference in activation energies, $E_p - {}^1/_2(E_t + E_t)$ or $E_p - E_t$, depending upon whether the initiation was slow or rapid, was calculated to be 6.6 ± 1.6 kcal./mole. Increasing the ratio, Al/Ti, caused slight decreases and increases in A and B, respectively.

In principle, an answer to the question as to whether the initiation was slow or rapid relative to the other steps, can be obtained from intrinsic viscosity measurements. For any polymerization in which transfer is significant we have

$$[n]^{1/a} = Q\,\bar{N}_n = Q\,\frac{\int_0^t R_p dt}{[C^*] + \int_0^t R_t dt + \int_0^t R_{tr} dt} \tag{6}$$

$$= K^{1/a}\bar{M}_v$$

where $\bar{N}_n$ is the number average degree of polymerization and R_p, R_t, and R_{tr} are the rates of propagation, termination, and transfer, respectively. For slow initiation this becomes

$$\frac{1}{[n]^{1/a}} = \frac{1}{Q}\left\{\frac{([M_0]/[M])^{1/A} - 1}{([M_0]/[M])^{1/A}(1 - [M]/[M_0])}\cdot\frac{[X_0]}{[M_0]} + \frac{k_{tr}[T]}{k_p[M_0]}\,\frac{\ln[M_0]/[M]}{1 - [M]/[M_0]}\right\} \tag{7}$$

and for fast initiation we obtain

$$\frac{1}{[n]^{1/a}} = \frac{1}{Q}\left\{\frac{[C_0^*]}{[M_0]}\,\frac{1}{1 - [M]/[M_0]} + \frac{k_{tr}[T]}{k_p[M_0]}\,\frac{\ln[M_0]/[M]}{1 - [M]/[M_0]}\right\} \tag{8}$$

where [T] is assumed to be independent of time and Q and a are 33×10^{-5} $\bar{N}_v/\bar{N}_n$ and 0.77, respectively, for *cis*-1,4 polybutadiene in benzene and are

assumed to be the same in toluene.[20] Since $A = 0.172$ in heptane at 2°C., differences between the two equations will be within the uncertainty of the experimental results for butadiene conversions greater than 15–20%. Hence estimates of $k_{tr}[T]/Qk_p$, $[C_0^*]/Q$, or $[X_0]/Q$ and their standard deviations were made by least mean squares using eq. (8) and the intrinsic viscosity-conversion results at monomer conversions greater than 15%.

TABLE IV
Effect of the Molar Ratios, Al/Ti and Ether/Al, on the Relative Rate Constants in Heptane at 2°C. at [Butadiene] = 2.28 moles/l., $[TiI_4] = 0.90 \times 10^{-3}$ moles/l.

Expt. no.	Al/Ti	Isopropyl ether/Al	A	$B[TiI_4]$	$k_{tr}[T]/Qk_p$	$[Co^*]/Q$
10	2.81	1.00	0.207 ± 0.005	1.5	0.19 ± 0.05	0.26
11	3.70	1.00	0.241 ± 0.01	2.5	0.95 ± 0.09	0.37
12	11.1	1.00	0.153	2.8	0.62 ± 0.04	0.41 ± 0.02
13	16.7	1.00	0.138	3.0	0.68 ± 0.04	0.32 ± 0.02
14	16.7	1.00	0.167 ± 0.006	3.3	0.54 ± 0.05	0.23
15	22.2	1.00	0.102 ± 0.009	10.0	0.51 ± 0.12	0.55
16	25.9	1.00	0.074 ± 0.003	10.0	0.87 ± 0.03	0.45
17	5.55	0.67	0.17	3.0	0.74 ± 0.02	0.23 ± 0.01
18	5.55	2.00	0.17	3.0	0.39 ± 0.04	0.63 ± 0.04

It appears that transfer was significant (Tables III and IV), and to fair approximations

$$k_{tr}[T]/Qk_p = 6.1[Al(i\text{-}C_4H_9)_3\text{etherate}]^{1/2}$$

$$\text{and } [C_0^*]/Q \text{ or } [X_0]/Q = 520[TiI_4]$$

If for these polymers $\bar{N}_w/\bar{N}_n$ was 2, the ratio of $[C_0^*]$ or $[X_0]$ to $[TiI_4]$ concentration was 0.33. The order of magnitude is reasonable for the case of soluble catalysts. With these results, the broken and solid portions of curves *C* and *D* in Figure 3 were calculated by eqs. (7) and (8), respectively, and the experimental results are in somewhat better agreement with the postulate that initiation was rapid. However, this evidence is not regarded as being conclusive. Relations between the intrinsic viscosity of greater than 30% conversion polymers and both the titanium tetraiodide and initial butadiene concentrations calculated by eq. (8) were also in good agreement with the experimental results (Figs. 4 and 5). Both $k_{tr}[T]/Qk_p$ and $[C_0^*]/Q$ or $[X_0]/Q$ were independent of temperature.

The results of the polymer fractionation experiments shown in Figure 6 substantiate the conclusion that transfer was significant. Otherwise, the molecular weight distributions would have been more broad than was observed, regardless of whether the initiation had been rapid or slow. For example, eq. (7) for slow initiation shows that at $A = 0.172$ the molecular weight of polymer formed at any instant would increase with increasing

conversion for negligible transfer which would cause the molecular weight distribution of the polymer to be more broad than the most probable. For the case of rapid initiation, the number-average and weight-average degrees of polymerization have been derived to be in the absence of transfer[22]

$$\bar{N}_n = \frac{[M_0] - [M]}{[C_0^*]} \tag{9}$$

which is obvious and

$$\bar{N}_w = \frac{\dfrac{2A[M_0]}{1 - 2A - [C_0^*]}\left\{1 - \dfrac{A}{1 - A}\left(\dfrac{[M]}{[M]_0}\right)^{(2A-1)/A} + \dfrac{2A - 1[M]}{1 - A[M_0]}\right\}}{1 - [M]/[M_0]} \tag{10}$$

For $A = 0.172$ and the conditions of experiments 3, 4, and 6, $\bar{N}_w/\bar{N}_n$ at 35 hr. reaction time was calculated to be 4.8, 4.8, and 3.7 respectively as opposed to the observed value of 2. Assuming and $\bar{N}_v = \bar{N}_w$ and $[C_0^*]/[TiI_4] = 0.33$, curves A and B in Figure 3 were calculated by eq. (10) to further demonstrate the role played by the transfer reaction.

Since the chemical structure of the catalytic species in this polymerization is not yet known, it is difficult to substantiate the proposed kinetic scheme with chemical evidence. An earlier polymerization study involving ethylene suggests that the bimolecular termination reaction may be due to the reduction of titanium to a lower oxidation state which is inactive and results in the cleavage of a polymer molecule from one of the metals of the catalyst complex.[13]

$$Ti^{4+}\bar{C}H_2CH_2(CH_2CH_2)_nR \rightarrow CH_2{=}CH(CH_2CH_2)_nR + 2Ti^{3+} + CH_3CH(CH_2CH_2)_nR$$
$$Ti^{4+}\bar{C}H_2CH_2(CH_2CH_2)_nR$$

These postulates are further supported by the recent report that alkyl titanium trichlorides are reduced by a bimolecular disproportionation reaction to yield an alkane–alkene mixture.[23]

The transfer reaction can be best explained by the assumption that unassociated $Al(i\text{-}C_4H_9)_{3-n}I_n$ is the transfer agent, the mechanism being similar to that postulated for the propylene polymerization.[10,11]

$$[Cat]^+{-}\bar{C}H_2CHCH_3(CH_2CHCH_3)_nR + R_1AlR_2 \rightarrow$$
$$[Cat]^+{-}\bar{R}_1 + R_2AlCH_2CHCH_3(CH_2CHCH_3)_nR$$

or

$$TiCl_nAlY_2P + AlR_3 \rightarrow TiCl_nAlR_3 + AlY_2P$$

Due to uncertainty about the catalyst-forming reaction, n is unknown. It is well established that trialkylaluminum and alkylaluminum halide com-

pounds form stable etherates and in the present system we will have the equilibrium

$$Al(i\text{-}C_4H_9)_{3-n}I_n + ROR \rightleftharpoons Al(i\text{-}C_4H_9)_{3-n}I_n \text{ etherate}$$

which is displaced far to the right.[24] When the molar ratio, ROR/AL, is constant, we obtain

$$[Al(i\text{-}C_4H_9)_{3-n}I_n] \propto [Al(i\text{-}C_4H_9)_{3-n}I_n \text{ etherate}]^{1/2} \propto k_{tr}[T]/k_p$$

Increasing the ether concentration would be expected to decrease the rate of chain transfer, and this was observed (Table IV).

The observation that the *cis* and *trans* contents of the polybutadienes depended upon the initial concentrations of the reagents whereas the vinyl content was constant indicates that more than one steric inversion process occurred. It has been postulated that inversion reactions that occur during the stereospecific polymerization of propylene are related to chain transfer phenomena, and the observed correlation between *cis* content and intrinsic viscosity of the polybutadiene suggests that this proposal might also be applicable to this polymerization.[11]

In conclusion, the proposed kinetic scheme accounts for the observations from polymerization rate, intrinsic viscosity, and molecular weight distribution measurements and it is unlikely to be seriously in error. The intrinsic viscosity results indicate, though not conclusively, that the initiation was rapid rather than slow relative to the other steps. Confirmation of this could be obtained both by very accurate measurements of intrinsic viscosity–butadiene conversion relations at low conversion and by the possession of more knowledge about the chemical mechanism of initiation.

Thanks are due to Dr. L. Breitman and Dr. M. Szwarc for helpful discussions, to Messrs. W. Congdon, A. P. Hobbs, J. M. Hulme, and V. V. Smith for their assistance in carrying out the experimental work, and to Polymer Corporation Limited for permitting this work to be published.

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Synopsis

An investigation of the kinetics of the butadiene polymerization by triisobutylaluminum diisopropyl etherate and titanium tetraiodide to yield predominantly *cis*-1,4 polymer was made by measuring the monomer conversion and the intrinsic viscosity of the polymer as functions of time. The molecular weight distributions of some of the polymers were determined by fractionation, and the ratio of weight-average to number-average molecular weight was about two. Polybutadiene microstructure determinations indicated that the vinyl content of polymer was independent of the experimental conditions but that the *cis* content decreased when the initial concentrations of butadiene and titanium tetraiodide were decreased and increased, respectively. This reaction can be described in kinetic terms by an initiation step which appears to be rapid relative to the propagation, by a termination step bimolecular in growing chains and by a transfer reaction whose rate was proportional to the half power of the concentration of triisobutyl-aluminum diisopropyl etherate.

Résumé

Une étude cinétique de la polymérisation du butadiène par l'éthérate diisopropylique du triisobutyle aluminium et le tétraiodure de titane en donnant essentiellement le polymère *cis*-1,4, fut abordée par des mesures de conversion du mononère et de la viscosité intrinsèque du polymère en fonction du temps. La détermination de la distribution des poids moléculaires de certains de ces polymères fut effectuée par fractionnement et le rapport du poids moléculaire en poids à celui en nombre fut trouvé environ égal à deux. Des déterminations de la microstructure du polybutadiène révèlent que le contenu en groupes vinyliques du polymère est indépendant des conditions expérimentales mais que le contenu en isomère *cis* décroît si les concentrations initiales en butadiène et en tétraiodure de titane décroissent et croissent respectivement. Cette réaction peut être décrite en termes cinétiques par une étape d'initiation qui semble rapide par rapport à la propagation, par une étape de terminaison bimoléculaire des chaînes croissantes et par une réaction de transfer dont la vitesse est proportionnelle à la demi-puissance de la concentration en diisopropyle éthérate de triisobutyle aluminium.

Zusammenfassung

Eine Untersuchung der Kinetik der Polymerisation von Butadien mit Triisobutylaluminium-Diisopropylätherat und Titantetrajodid unter vornehmlicher Bildung von *cis*-1,4-Polymerem wurde durch Messung des Monomerumsatzes und der Viskositätszahl des Polymeren als Funktion der Reaktionsdauer durchgeführt. Die Molekulargewichtsverteilung einiger Polymerer wurde durch Fraktionierung bestimmt und das Verhältnis Gewichts- zu Zahlenmittel des Molekulargewichts ergab sich zu etwa zwei.

Die Bestimmung der Mikrostruktur des Polybutadiens zeigte, dass der Vinylgehalt des Polymeren unabhängig von den Versuchsbedingungen ist, dass jedoch der *cis*-Gehalt bei Herabsetzung der Ausgangskonzentration des Butadiens und Erhöhung derjenigen des Titantetrajodids abnimmt. Die Reaktion kann kinetisch durch einen im Vergleich zum Wachstum reschen Startschritt, einen Kettenabbruch zweiter Ordung in bezug auf die wachsenden Ketten und eine Übertragungsreaktion mit einer zur Potenz ein halb der Triisobutylaluminium-Diisopropylätherat-Konzentration proportionalen Geschwindigkeit beschrieben werden.

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La Mesure des Vitesses de Polymérisation de l'Isoprène en Présence de Lithium Métallique

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Un nouvel appareil de mesure des vitesses de polymérisation de l'isoprène, utilisant le phénomène de contraction des monomères est décrit. On donne les résultats de deux séries de mesures.

I. DESCRIPTION DE L'APPAREIL

Le monomère est introduit sans bulles dans un manchon en pyrex. Le lithium en grains est laminé de façon continue entre la paroi interne du manchon et un barreau magnétique roulant le long de cette paroi.

Les Figures 1 et 2 montrent les différents détails. Un capillaire dont le diamètre intérieur sera fonction de la concentration en isoprène et du taux de conversion désiré, muni à sa base d'une gaine métallique G, est fixé à l'aide d'une vis de pression P sur un système mobile S comprenant un soufflet S′, le tout en acier inoxydable. Le soufflet étant rempli de mercure très pur, le capillaire est fixé définitivement sur le système mobile S.

Ce dernier peut être monté ou abaissé dans une vis V servant de presse-étoupe, elle-même fixée dans un bloc I en acier inoxydable comprenant deux vannes X et X′. Ces deux vannes ont été construites de manière à éviter tout volume mort.

Le système mobile S sert à ajuster le niveau de la colonne de mercure au début de chaque mesure. Cette mise à zéro s'effectue sans arrêter le laminage.

Le laminage du catalyseur se fait entre la paroi du manchon M et le barreau magnétique B. Celui-ci est entraîné par un aimant extérieur A placé entre le manchon M et les tiges permettant le serrage du manchon. La distance entre l'aimant et le manchon est réglable. Ce système a pour avantage de mieux laminer le lithium d'où une meilleure reproductibilité des mesures.

La plaque en acier inoxydable F qui ferme le fond du manchon M est munie d'un tube creux T, dans lequel circule un liquide à la température choisie, permettant d'une part d'atteindre beaucoup plus rapidement

l'équilibre de température, et d'autre part d'évacuer rapidement la chaleur réactionnelle.

La Figure 3 représente le montage utilisé pour l'enregistrement des courbes de contraction. Elles sont suivies par une mesure de la résistance d'un fil de platine P tendu à l'intérieur du capillaire. Cette résistance augmente au fur et à mesure qu'une partie plus importante du fil de

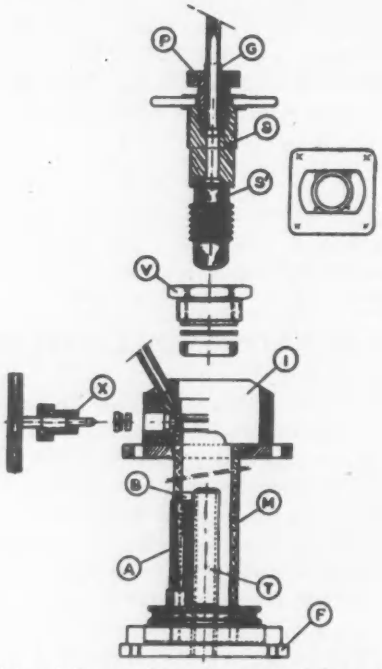

Fig. 1. Schéma de l'appareil pour la mesure de la contraction.

platine émerge du mercure. Pour faire cette mesure, on détermine la variation de la différence de potentiel aux bornes du conducteur, quand celui-ci est monté dans un circuit électrique alimenté par un accumulateur de 4 volts. La résistance totale du circuit, 12.000 ohms, a été calculée pour que l'intensité du courant puisse être considérée comme constante au cours des mesures, l'augmentation de la résistance du fil de Pt étant toujours inférieure au millième de la résistance totale. Un potentiomètre automatique permet d'enregistrer la variation de la différence de potentiel pendant toute la durée de l'expérience.

II. TECHNIQUE DE REMPLISSAGE

Le catalyseur sous forme d'émulsion de lithium dans la vaseline est déposé sur la paroi interne du manchon en pyrex et exactement pesé.

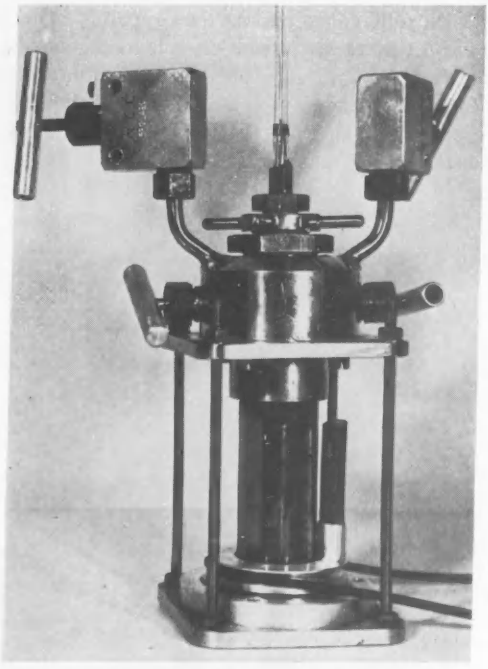

Fig. 2. Appareil pour la mesure de la contraction.

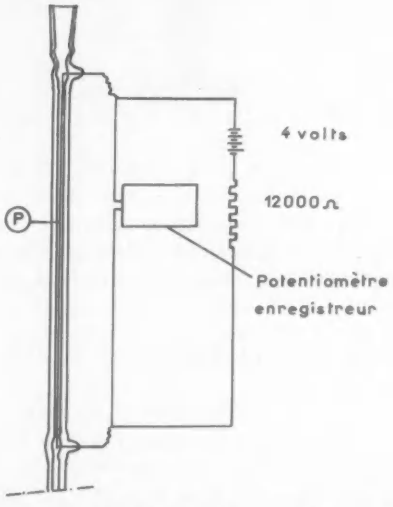

Fig. 3. Schéma du dispositif d'alimentation électrique et d'enregistrement.

On assemble les différentes parties de l'appareil. On tare l'appareil vide et il est raccordé au récipient contenant le monomère en solution dans un hydrocarbure aliphatique ou aromatique par l'intermédiaire d'un T (Fig. 4). On fait le vide dans le manchon M, puis le liquide est admis à la température ordinaire. On arrête le transvasement quand on n'observe plus de bulles de gaz dans le manchon.

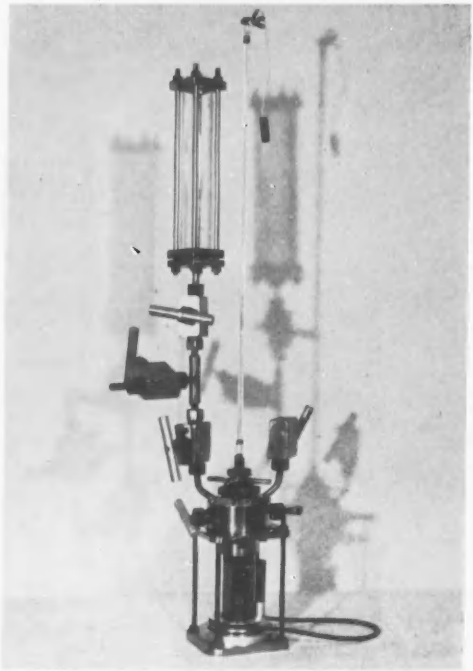

Fig. 4. Dispositif pour le remplissage du récipient de polymérisation.

Cet appareil permet aussi d'envisager la mesure des vitesses de polymérisation de l'isoprène en présence de butyllithium ou tout autre catalyseur en solution, le barreau magnétigue servant alors d'agitateur.

III. DESCRIPTION DE L'ETUVE

La mise à la température de l'étuve se fait au moyen d'un courant d'air produit par deux turbines M et N passant sur un radiateur R à grande surface, dans lequel circule un liquide provenant d'un thermostat dont la température peut varier de $-20°C$ à $+50°C$. Le radiateur est branché en série avec le tube T′ pour les raisons indiquées précédemment (Fig. 5).

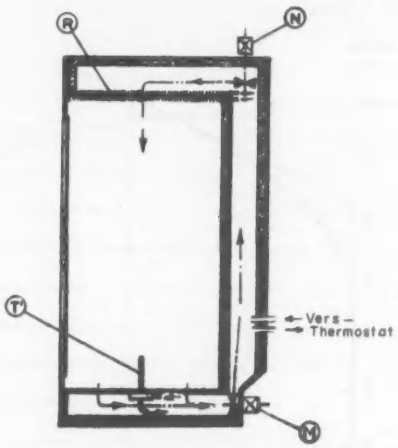

Fig. 5. Schéma de l'étuve.

IV. TECHNIQUE DE MESURE

Tant que le laminage n'entre pas en action, le catalyseur reste enrobé de vaseline et il est peu actif.

L'équilibre de température de l'appareil de cinétique étant atteint, on ajuste le niveau du mercure à la partie supérieure du capillaire et on met en marche le laminage. La contraction qui accompagne la polymérisation fait descendre la colonne de mercure et on enregistre la variation de la chute de potentiel correspondante. Arrivé au bout du capillaire, on peut remettre au niveau initial, à l'aide du système mobile S.

V. RESULTATS

La détermination de la vitesse de disparition du monomère $-d[M]/dt$ à partir de mesures dilatométriques nécessite la connaissance de la variation du volume molaire inhérente à la réaction de polymérisation. Nous avons calculé la variation du volume molaire à partir des volumes spécifiques de l'isoprène et du polyisoprène, le volume spécifique du polyisoprène ayant été lui-même mesuré par un extrait sec fait immédiatement sur le mélange réactionnel après arrêt de la polymérisation. Nous avons trouvé la valeur de 1,077 ml/g, qui se rapproche de celle donnée pour le caoutchouc d'hévéa (1,088 ml/g), dont la structure (97,8% *cis*-1,4) est sensiblement identique à celle (plus de 90% *cis*-1,4) du polyisoprène préparé par initiation avec le lithium.

La Figure 6 montre l'allure des courbes obtenues par enregistrement. On y voit que la vitesse de polymérisation devient pratiquement constante à partir d'un taux de conversion d'environ 9%. Dans le Tableau I et sur la Figure 7, on trouvera reportées les vitesses de polymérisation en

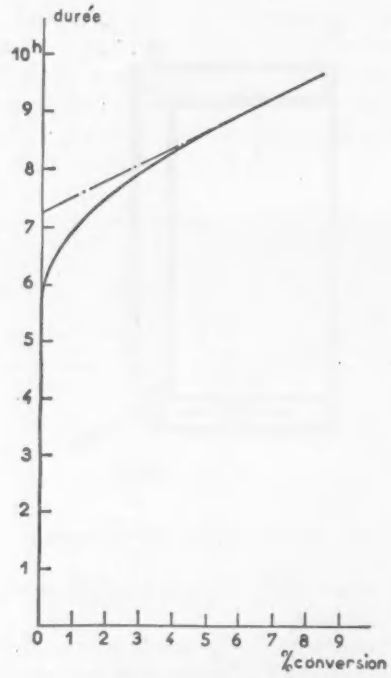

Fig. 6. Vitesse de polymérisation de l'isoprène en présence de lithium métallique.

solution obtenues à différentes concentrations en lithium, la concentration en isoprène restant constante.

Dans le Tableau II et sur la Figure 8 on a donné les résultats de trois polymérisations en masse. Rappelons que dans ce cas, il est difficile de

TABLEAU I

Concentration isoprène, mole/l	Concentration Li, mole/l	Période d'induction, h	Température de polymérisation, °C	$-d[M]/dt$ = quantité d'isoprène disparue, mole/l/min) $\times 10^{-4}$
1,07	0,03	8	30	3,9
1,23	0,07	7,25	30	5,8
1,23	0,10	7,5	30	6,4
1,21	0,14	5,67	30	7,2
1,17	0,20	3	30	7,6
1,17	0,20	2,5	30	7,4
1,17	0,23	3,5	30	8,5
1,12	1,30	1,75	30	10,2

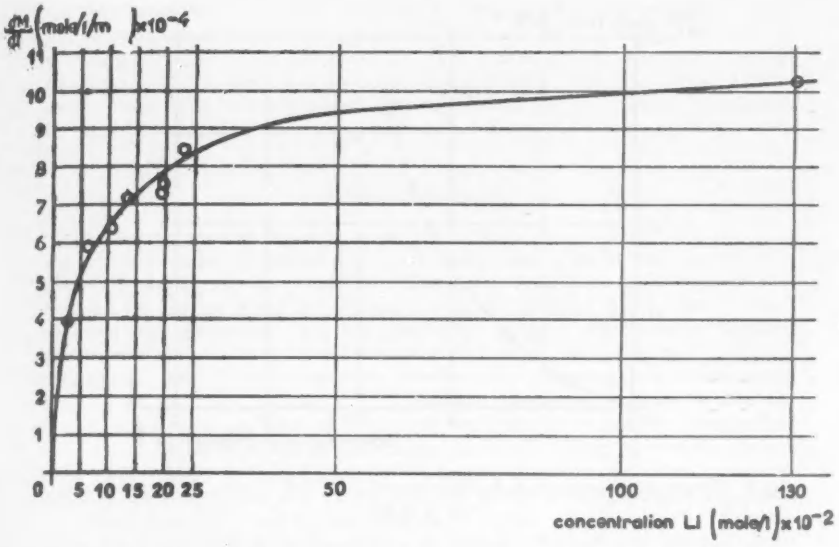

Fig. 7. Vitesse de polymérisation de l'isoprène en solution en fonction de la concentration en lithium.

dépasser quelques pourcents de conversion, par suite de la viscosité rapidement croissante du milieu et par suite de l'élévation de la température. Les vitesses données sont celles obtenues après environ 1% de conversion.

TABLEAU II

Concentration isoprène, mole/l	Concentration Li, mole/l	Période d'induction, h	Température de polymérisation, °C	$-d[M]/dt$ = quantité d'isoprène disparue, mole/l/min) $\times 10^{-4}$
9,83	0,006	20	30	2,5
9,83	0,014	0,67	30	7,4
9,83	0,028	3	30	32

La période d'induction (mesurée entre le début du laminage et le commencement de la variation de volume) très variable semble toutefois diminuer quand la concentration en lithium augmente.

La reproductibilité des périodes d'induction et des vitesses de polymérisation en présence de dispersions de Li exige un mode opératoire (principalement dans le séchage des réacteurs, du monomère et du solvant) d'autant plus rigoureusement respecté que la concentration en Li est plus petite.

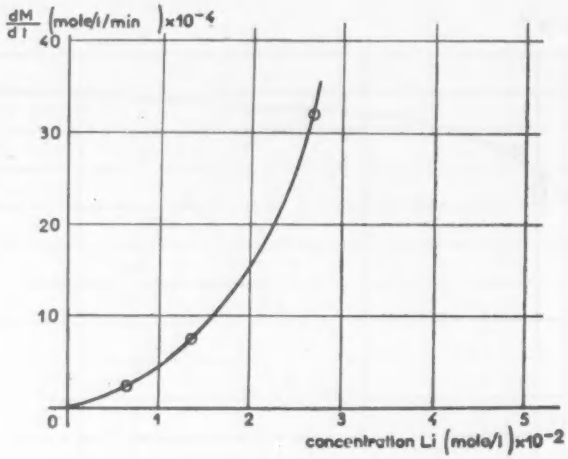

Fig. 8. Vitesse de polymérisation de l'isoprène en masse en fonction de la concentration en lithium.

Les auteurs tiennent à remercier M. C. Ortlieb pour ses précieux conseils et M. Th. Wolff pour son aide dans la réalisation des divers montages.

Résumé

Un nouvel appareil de mesure des vitesses de polymérisation de l'isoprène, utilisant le phénomène de contraction des monomères, est décrit. Le monomère est introduit sans bulles dans un manchon en pyrex. Le lithium en grains est laminé de façon continue entre la paroi interne du manchon et un barreau magnétique roulant le long de cette paroi. Un soufflet en acier inoxydable, rempli de mercure et surmonté d'un capillaire, se trouve au contact du monomère. L'enregistrement des courbes de contraction est suivi par une mesure de la résistance d'un fil de platine situé dans le capillaire. Cette résistance augmente au fur et à mesure qu'une partie plus importante du fil de platine émerge du mercure. Afin d'effectuer ces mesures dans de bonnes conditions, le mercure doit être toujours propre. Il faut aussi assurer une bonne stabilité de la température du récipient de polymérisation, pour éviter tout effet parasite dû à une dilatation ou une contraction thermique du mélange réactionnel. Dans une première série de mesures nous avons déterminé les vitesses de polymérisation en solution obtenues à différentes concentrations en lithium, la concentration en isoprène restant constante. Dans une deuxième série de mesures nous avons déterminé les vitesses de trois polymérisations en masse.

Synopsis

A new apparatus for measuring the rate of polymerization of isoprene has been described, using the volume contraction of the monomers. The monomer is introduced without bubbles in a pyrex-tube. Lithium grains are continuously laminated between the inside wall of the vessel and a magnetic road moving along the wall. A stainless steel valve, filled with mercury and carrying a capillary tube, is in contact with the monomer. The registration of the curves of contraction is followed by measuring the resistance of a platina-wire located in the capillary. This resistance increases when the length of the wire emerging from the mercury increases. In order to carry

out these measurements in good conditions, the mercury must be kept always clean. The polymerization vessel must be carefully thermostatized in order to prevent any secundary effect due to any thermal dilatation or contraction of the reaction mixtures. In a first series of measurements the rates of solution polymerization at different lithium concentration have been determined, keeping constant the concentration of isoprene. In a second series, the rates were measurements for three bulk polymerization experiments.

Zusammenfassung

Ein neuer Apparat zur Bestimmung der Polymerisationsgeschwindigkeit des Isoprens aus der Kontraktion des Monomeren wird beschrieben. Das Monomere wird ohne Blasen in ein Pyrexgefäss eingeführt. Das gekörnte Lithium wird kontinuierlich zwischen der inneren Wand des Gefässes und einem an dieser Wand rollenden magnetischen Stab gequetscht. Ein mit Quecksilber gefüllter und mit einer Kapillare versehener Bahälter aus nichtoxydierbarem Stahl befindet sich in Kontakt mit dem Monomeren. Die Kontraktionskurven werden durch Messung des Widerstandes eines in der Kapillare befindlichen Platinfadens aufgenommen. Dieser Widerstand nimmt um so mehr zu, ein je grösserer Teil des Platinfadens aus dem Quecksilber herausragt. Um diese Messungen einwandfrei ausführen zu können, muss das Quecksilber immer rein sein. Auch eine gute Temperaturkonstanz des Polymerisationsgefässes muss sichergestellt sein, um unerwünschte Effekte durch thermische Dilatation oder Kontraktion der Reaktionsmischung zu vermeiden. In einer ersten Messreihe wurde die Polymerisationsgeschwindigkeit in Lösung bei konstanter Isoprenkonzentration in Abhängigkeit von der Lithiumkonzentration bestimmt. In einer zweiten Messriehe wurde die Geschwindigkeit von drei in Substanz durchgeführten Polymerisationen gemessen.

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La Mesure des Vitesses de Polymérisation du 2,3-Diméthyl-1,3-butadiène en Présence de Lithium Métallique

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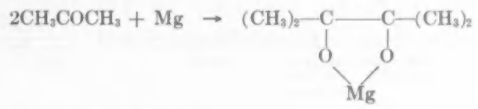
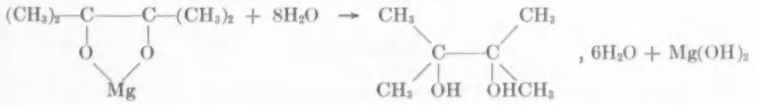
La préparation du dimethylbutadiène et purification par sulfonation et la mesure des vitesses de polymérisation du diméthylbutadiène, en solution dans le pentane, en présence de lithium métallique sont décrites. On donne les résultats de deux séries de mesures.

PARTIE THÉORIQUE

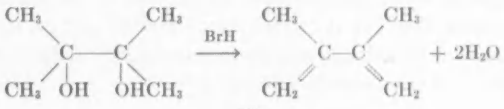
Préparation du 2,3-Diméthyl-1,3-butadiène

Le diméthylbutadiène a été préparé en deux étapes à partir de l'acétone, d'après les méthodes publiés.[1] Dans une première étape, la réduction duplicative de l'acétone par un amalgame de magnésium fournit le pinacol hydraté à 6 molécules d'eau. Ce dernier est obtenu anhydre par distillation en présence de benzène (élimination d'un mélange benzène + eau).



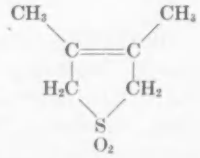


Dans une deuxième étape, on obtient le diméthylbutadiène par deshydratation du pinacol anhydre en présence de BrH.



Purification du 2,3-Diméthyl 1,3-butadiène

La sulfonation, méthode utilisée généralement pour la purification des diènes conjugés et permettant l'obtention de corps extrêmement purs, a été employée ici. En effet, l'anhydride sulfureux liquide réagit avec les diènes conjugués pour donner une sulfone cyclique. Dans le cas du diméthylbutadiène, nous obtenons du 3,4-diméthyl-2,5-dihydro-thiophène-dioxyde:[2]



Par chauffage à 120–130°C dans l'appareil representé sur la Figure 1 cette sulfone se décompose pour redonner le diméthylbutadiène pur.

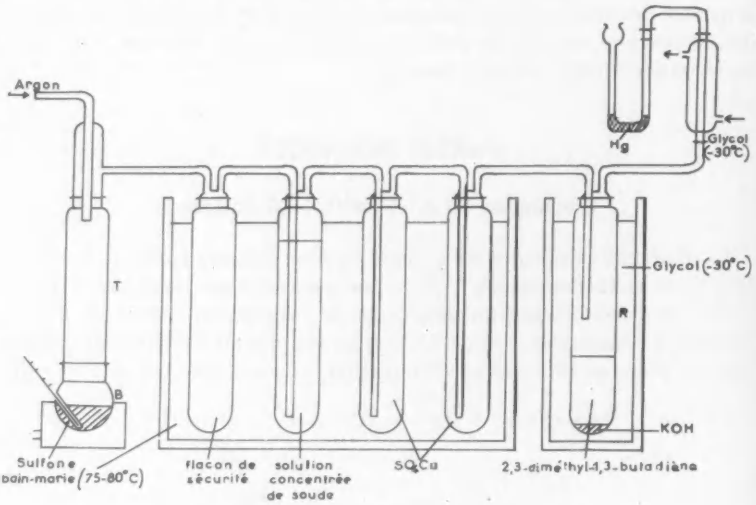


Fig. 1. Régénération du diméthylbutadiène.

Résultats

La détermination de la vitesse de disparition du monomère $-d[M]/dt$ à partir de mesures dilatométriques nécessite la connaissance de la variation du volume molaire inhérente à la réaction de polymérisation. Nous avons calculé la variation du volume molaire à partir des volumes spécifiques du diméthylbutadiène et du polydiméthylbutadiène, le volume spécifique du polydiméthylbutadiène ayant été lui-même mesuré par un extrait sec fait immédiatement sur le mélange réactionnel après arrêt de la polymérisation. Nous avons trouvé la valeur de 1,11 ml/g.

La Figure 2 montre l'allure des courbes obtenues par enregistrement. On y voit que la vitesse de polymérisation devient pratiquement constante à partir d'un taux de conversion d'environ 10%.

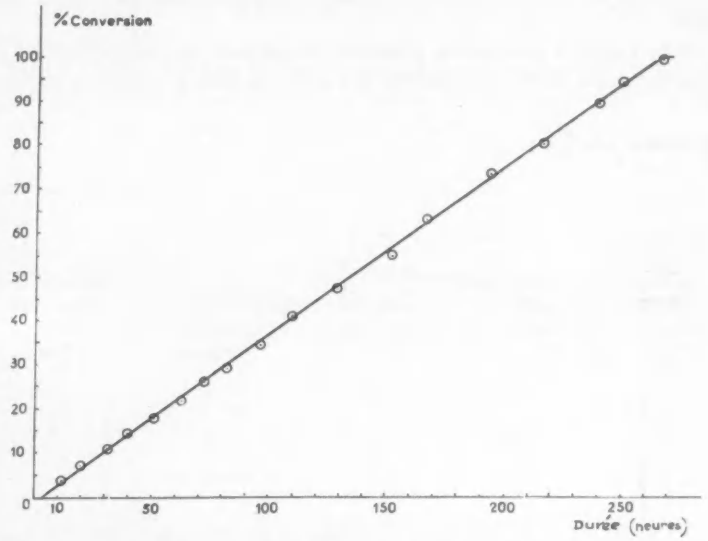


Fig. 2. Vitesse de polymérisation du 2,3-diméthyl-1,3-butadiène en présence de lithium métallique.

Dans le Tableau I et sur la Figure 3, on trouvera rèportées les vitesses de polymérisation en solution dans le pentane, obtenues à différentes concentrations en lithium, la concentration en diméthylbutadiène restant constante. Les vitesses données sont celles obtenues après 10% de conversion.

TABLEAU I

Concentration dimethyl-butadiène, mole/l	Concentration lithium, mole/l	Période d'induction, h	Température de polymérisation, °C	$-d[M]/dt$, quantité de dimethyl-butadiène disparue, (mole/l/min) $\times 10^{-4}$
1,3	0,05	27	30	0,4
1,3	0,11	25	30	0,5
1,3	0,18	—	30	0,5
1,3	0,18	—	30	0,6
1,3	0,36	—	30	0,7
1,3	0,75	13	30	0,8
1,3	1,52	3	30	0,8

On constate que la vitesse, croissant très rapidement pour de très faibles concentrations en lithium (0,05–0,03 mole/l), atteint un palier de 0,8 × 10^{-4} mole/l/min pour une concentration de 0,75 mole/l. La période d'induction (mesurée entre le début du laminage et le commencement de la variation de volume) diminue quand la concentration en lithium augmente.

Sur la Figure 4 nous avons comparé les vitesses de polymérisation de l'isoprène et du diméthylbutadiène (en solution dans le pentane) en fonc-

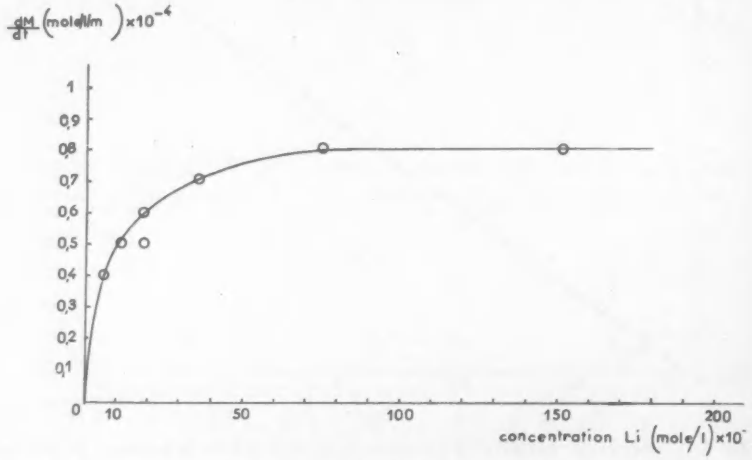


Fig. 3. Vitesse de polymérisation du diméthylbutadiene en solution en fonction de la concentration en lithium.

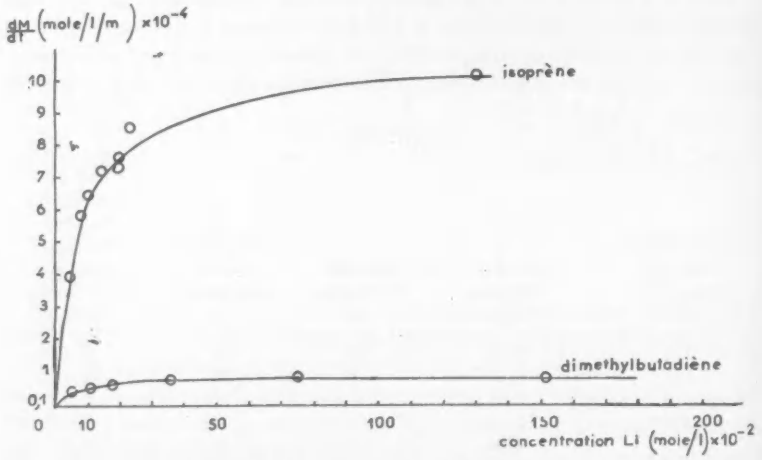


Fig. 4. Comparaison des vitesses de polymérisation de l'isoprène et du diméthylbutadiène en solution en fonction de la concentration en lithium.

tion de la concentration en lithium, pour des concentrations en isoprène et en dimethylbutadiène constantes et égales. La vitesse limite de polymérisation de l'isoprène est dix fois plus grande que celle du dimethylbutadiène. On pourrait penser à priori que cet écart est lié à la différence d'encombrement due à la présence d'un deuxième groupement méthyl, des deux molécules.

Dans le Tableau II et sur la Figure 5 sont donnés les résultats des vitesses de polymérisation en solution dans le pentane à différentes concentrations

TABLEAU II

Concentration diméthyl-butadiène, mole/l	Concentration lithium, mole/l	Période d'induction, h	Température de polymérisation, °C	$-d[M]/dt$, quantité de dimethyl-butadiène disparue, (mole/l/min) $\times 10^{-4}$
3,17	0,18	2	30	3,8
2,12	0,18	6	30	2,2
1,28	0,18	—	30	0,6
0.36	0,18	34	30	0,2

en diméthylbutadiène, la concentration en lithium restant constante. La période d'induction diminue quand la concentration en dimethylbutadiène augmente.

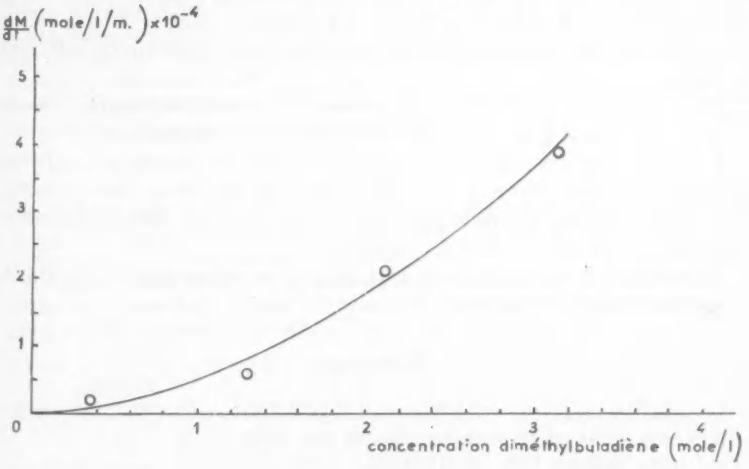


Fig. 5. Vitesse de polymérisation du diméthylbutadiène en solution dans le pentane en fonction de sa concentration initiale.

PARTIE EXPÉRIMENTALE

Préparation et Purification de la Sulfone

La préparation de la sulfone est analogue à celle de la sulfone de l'isoprène.[3]

On utilise un autoclave de 500 ml en acier inoxydable, muni d'une vanne à pointeau permettant l'élimination des gaz n'ayant pas réagi. Après refroidissement avec de la carboglace, il est chargé successivement de 136 ml de diméthylbutadiène, 65 ml de méthanol, 4 g de *p-tert*-butylcatechol, et de 80 ml d'anhydride sulfureux liquide.

L'autoclave est fermé, puis chauffé lentement à 85°C et maintenu à cette température pendant cinq heures. La présence de *p-tert*-butylcatechol diminue considérablement la formation de polysulfone et de ce fait augmente donc le rendement en sulfone.[2]

Le rendement en sulfone par rapport au diméthylbutadiène est d'environ 80%.

Par recristallisations successives de la sulfone dans l'alcool méthylique, on obtient une substance cristalline incolore.

Régénération du Diméthylbutadiène

La sulfone purifiée est décomposée dans le montage représenté Figure 1.

Un ballon B contenant la sulfone est surmonté d'un tube T de grande section destiné à éviter toute obstruction due à la sublimation de la sulfone.

Le dimethylbutadiène régénéré passe d'abord dans une solution concentrée de soude absorbant l'anhydride sulfureux, puis sur deux colonnes désséchantes (SO_4Ca) avant d'être recueilli dans un flacon récepteur R plongeant dans du glycol à −30°C. La potasse contenue dans le flacon récepteur est destinée à absorber les dernières traces d'anhydride sulfureux et d'eau.

Cette régénération est faite sous atmosphère inerte, la présence d'azote et d'oxygène étant gênante par la suite pour la polymérisation.

Le monomère ainsi purifié est mis au contact de lithium en paillettes pendant quelques heures. On élimine ainsi les dernières traces d'azote, d'oxygène et d'eau pouvant perturber la cinétique de polymérisation et empêcher la reproductibilité des mesures.[4]

En vérifiant la pureté par chromatographie en phase gazeuse, on décèle au maxium 0,01% d'impureté.

References

1. *Organic Syntheses, Coll. Vol. II*, p. 459; *Organic Syntheses, Coll. Vol. III*, p. 312.
2. Staudinger, H., et Ritzenthalter, *Ber.*, **68**, 469 (1935).
3. *Organic Syntheses, Coll. Vol.* III, p. 499.
4. Ortlieb, C., Th. Wolff, J. Marchal., et A. Hinschberger, *Rev. gén. Caoutchouc*, **37**, 825 (1960).
5. Schué, F., A. Hinschberger, et J. Marchal, *Rev. gén. Caoutchouc*, **39**, 572 (1962).

Résumé

Le 2,3-dimethyl-1,3-butadiène a été préparé à partir de l'acétone. La sulfonation, méthode utilisée généralement pour la purification des dienes conjugés et permettant l'obtention de corps extrêmement purs, a été employée ici. En effet, l'anhydride sulfureux liquide réagit avec le dimethylbutadiène pour donner une sulfone cyclique. Par recristallisations successive de cette sulfone dans l'alcool méthylique on obtient une substance cristalline incolore qui par chauffage à 120–130°C se décompose quantitativement pour redonner le dimethylbutadiene pur. Deux séries de mesures ont été faites: (*1*) les vitesses de polymérisation en solution dans le pentane obtenues à différentes condentrations en lithium, la concentration en diméthylbutadiéne restant constante; (*2*) les vitesses de polymérisation en solution dans le pentane à différentes concentrations en diméthylbutadiène, la concentration en lithium restant constante.

Synopsis

2,3-Dimethyl-1,3-butadiene has been prepared from acetone with the sulfonation method, generally used for the high purification of conjugated dienes. Indeed liquid sulfur oxide reacts with dimethylbutadiene and gives a cyclic sulfon. After repeated crystallization of this sulfon in methanol, a colorless substance is obtained that by heating at 120–130°C. decomposes quantitatively in pure dimethylbutadiene. Two series of measurements have been carried out: (*1*) polymerization rates in pentane solution at different lithium concentration, keeping constant the concentration of dimethylbutadiene, (*2*) polymerization rates in pentane solution at different monomer concentration keeping the lithium concentration constant.

Zusammenfassung

Ausgehend von Aceton wurde 2,3-Dimethyl-1,3-butadien dargestellt. Die Sulfonierung, eine allgemein zur Reinigung konjugierter Diene angewendete Methode, die Gewinnung extrem reiner Substanzen gestattet, wurde hier benützt. Tatsächlich liefert flüssiges Schwefeldioxyd mit Dimethylbutadien ein cyklisches Sulfon. Durch mehrfache Umkristallisation dieses Sulfons aus Methylalkohol gewinnt man eine farblose, kristalline Substanz, die sich beim Erhitzen auf 120–130°C quantitativ unter Rückbildung von reinem Dimethylbutadien zersetzt. Zwei Versuchsreihen wurden durchgeführt: (*1*) Polymerisationsgeschwindigkeit in Pentanlösung bei verschiedenen Lithiumkonzentrationen und konstanter Dimethylbutadienkonzentration. (*2*) Polymerisationsgeschwindigkeit in Pentanlösung bei verschiedener Dimethylbutadienkonzentration und konstanter Lithiumkonzentration.

Discussion

K. F. O'Driscoll (*Villanova University, Penna.*): In similar work with styrene, we have always observed sigmoidal time-conversion curves. Have you any explanation for the linear curve you show for dimethylbutadiene?

F. Schué: Nous avons toujours observé une forme sigmoide des courbes % conversion-temps dans la polymèrisation du diméthylbutadiène. Mais cette forme n'apparait pas sur la Figure 2 en raison de l'échelle des temps adoptée.

JOURNAL OF POLYMER SCIENCE: PART C NO. 4, PP. 267-279

Synthesis of Optically Active Polymers by Asymmetric Catalysts. I. Mechanism of Propylene Oxide Polymerization Induced by Asymmetric Catalyst

TEIJI TSURUTA, SHOHEI INOUE, MICHIHIRO ISHIMORI, and NORIMASA YOSHIDA, *Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Kyoto, Japan*

INTRODUCTION

We reported previously[1,2] that diethylzinc induces the stereospecific polymerization of propylene oxide at room temperature in the presence of a suitable quantity of water or alcohol. Infrared studies on the reaction products of diethylzinc with several alcohols indicated the active species of the diethylzinc–alcohol system to be zinc dialkoxide, $Zn(OR)_2$.

If a binary system consisting of diethylzinc and optically active alcohol is used as polymerization catalyst, the zinc dialkoxide having asymmetric centers is expected to produce an optically active poly(propylene oxide). We have confirmed[3,4] this by experiments in which (+)-borneol or (−)-menthol was used as alcohol component in the catalyst system.

This paper presents results of experiments on the propylene oxide polymerization induced by an asymmetric catalyst. In the light of these results, the reaction mechanism of the stereoregular polymerization of propylene oxide is discussed.

EXPERIMENTAL

Materials

Diethylzinc was prepared by the standard method[5] and purified by fractional distillation under reduced pressure.

Primary alcohols were dried by refluxing over magnesium ribbon. Secondary and tertiary alcohols were dried by refluxing over barium oxide. After drying, the alcohols were fractionated through a 50-cm. Vigreux column and the middle fractions of each were taken.

Commercial borneol was treated with zinc chloride in benzene to remove isoborneol followed by recrystallization from hexane,[6] m.p. 203.5–204.0°C. (uncorr.), $[\alpha]_D = +36°$, $c = 2.07$ in ethanol.

Propylene oxide (racemic) was refluxed over potassium hydroxide pellets and subsequently dried over calcium hydride. It was fractionally distilled through a 50-cm. Vigreux column, and the middle fraction was taken.

Heptane and hexane were refluxed over calcium hydride and fractionally distilled. Toluene was refluxed over metallic sodium and fractionally distilled.

Infrared Spectra

The infrared spectra were measured with a Nipponbunko IR-S double-beam spectrometer with NaCl prisms or a Hitachi EPI-2 double-beam spectrometer with a KBr prism at room temperature. A liquid cell with KBr windows was used for observing the spectra concerned with C-Zn and O-Zn bonds in the catalyst system. The rate of decrease of alcohol concentration in the diethylzinc–alcohol system in heptane or hexane solution was traced by using a liquid cell with NaCl windows. Since dialkylzinc and its reaction products are very susceptible to moisture and oxygen, the samples were handled under purified argon throughout the infrared measurement.

Polymerization of Propylene Oxide

A heptane solution of diethylzinc–alcohol system was prepared in a test tube after flushing with argon, whereupon a definite quantity of propylene oxide was added. The tube was sealed and placed in a constant temperature bath at 30° ± 0.5°C. Also, the same experiment was done at 80° ± 0.5°C. In the case of (+)-borneol as alcohol component, polymerization was carried out in toluene at 70°C. After a definite time, the reaction mixture was diluted by a larger volume of toluene or benzene. From the reaction mixture, unreacted monomer and solvent were distilled off *in vacuo* and collected in a cold trap immersed in Dry Ice–ethanol. The collected mixture was distilled to recover unreacted monomer. (b.p., 35°C.); the infrared spectrum of the recovered monomer was identical to that of the racemic monomer used as the starting material.

RESULTS AND DISCUSSION

Active Species of the Catalyst System

The reaction of diethylzinc with alcohol is considered to proceed according to the following equations:

$$\mathrm{EtZnEt + ROH \rightarrow ROZnEt + EtH} \quad (1)$$

$$\mathrm{ROZnEt + ROH \rightarrow ROZnOR + EtH} \quad (2)$$

Reactions (1) and (2) can be followed by measuring the decrease in the infrared absorption of OH group in the reaction system with time. Figure 1 shows an example with methanol. As can be seen from Figure 1, there was observed a sudden disappearance of 50% of the methanol when one mole of diethylzinc was treated with two moles of methanol, but the remaining 50% methanol disappeared very slowly. The result may suggest that the reaction (1) takes place very rapidly, whereas the reaction (2) proceeds slowly. Since the measurement of OH absorption is a rather indi-

rect method for studying the reaction of diethylzinc with alcohol, we adopted a direct method, in which the formation and disappearance of O—Zn and C—Zn bonds were measured in the KBr region as shown in Figure 2.

Characteristic absorptions of diethylzinc are 618 and 564 cm.$^{-1}$. In the 1:1 diethylzinc–methanol reaction system (No. 2), two new absorption bands appeared at 519 and 405 cm.$^{-1}$. An absorption at 610 cm.$^{-1}$ in No. 2 is considered to have shifted from 618 cm.$^{-1}$ in No. 1.

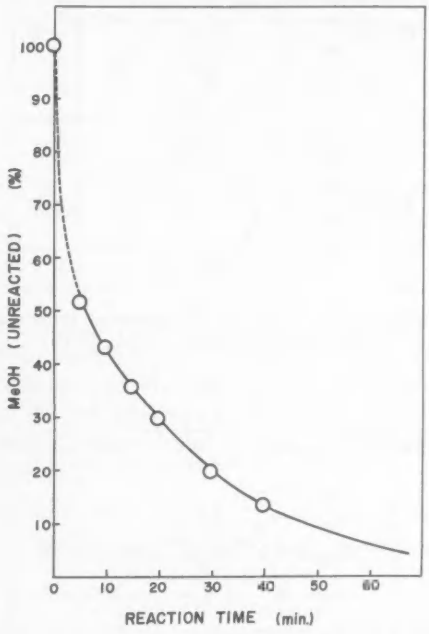


Fig. 1. Decrease in rate of reaction of methanol in the $ZnEt_2$–MeOH system (MeOH/$ZnEt_2$ = 2.0, $ZnEt_2$ 0.01M, n-hexane 10 ml.).

In the case of the 1:2 diethylzinc–methanol reaction system, a marked change in the infrared absorptions with time was observed, which was not the case with the 1:1 system. The change of the infrared absorption with time is shown in Figure 3.

It is of interest to note that the infrared spectrum of No. 2 in Figure 2 is almost identical with that of No. 1 in Figure 3, in spite of the significant difference in the activity of the two catalyst systems. We have confirmed that the intensity of the bands at 552 and 470 cm.$^{-1}$ increased at the expense of the band at 610 cm.$^{-1}$. Furthermore, the increasing rates of band absorptions at 552 and 470 cm.$^{-1}$ were found to run parallel with the decreasing rate of OH group absorption.

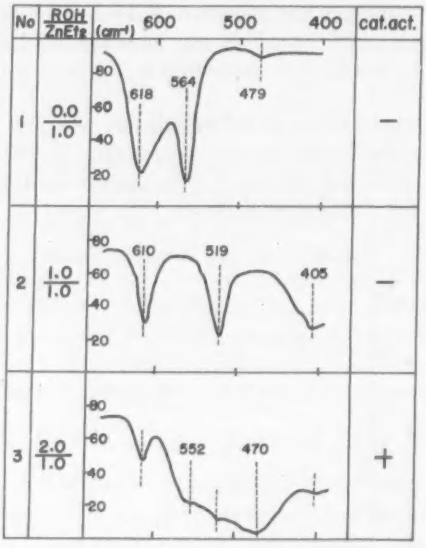


Fig. 2. Infrared spectra of the $ZnEt_2$–MeOH system at three different mole ratios ($ZnEt_2$ 0.005M, n-heptane 15 ml., 30°C.).

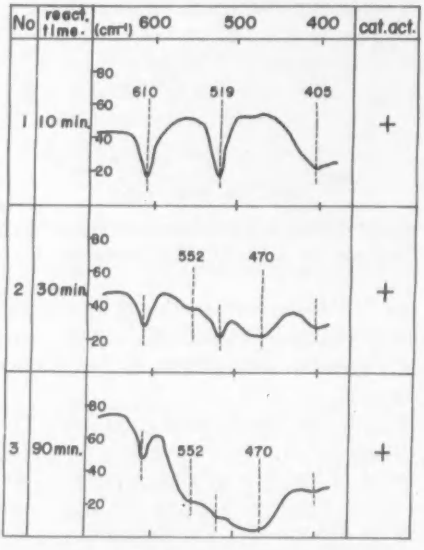


Fig. 3. Infrared spectra of the $ZnEt_2$–MeOH system at three different reaction times ($MeOH/ZnEt_2 = 2$).

Tentative assignments of infrared bands in the reaction system of diethylzinc with methanol are listed in Table I. More detailed results will be presented;[8]

TABLE I
Tentative Assignments of Infrared Bands in the Reaction System of Diethylzinc with Methanol

Wave number, cm.$^{-1}$	$ZnEt_2$	EtZnOMe	$Zn(OMe)_2$	Assignment[a]
618	Yes			
			No	$\gamma_r(CH_2)$
610		Yes		
564	Yes	No	No	ν_a(C—Zn—C)
552	No	No	Yes	ν(O—Zn—O)
519	No	Yes	No	ν_a(C—Zn—O)
470	No	No	Yes	ν(O—Zn—O)
(420) 405	No	Yes	No	ν_s(C—Zn—O)

[a] $\gamma_r(CH_2)$ = rocking, γ_s = symmetric stretching, ν_a = antisymmetric stretching.

These results obviously indicate that the rate of reaction (1) is much larger than that of reaction (2). Reactions of diethylzinc with several alcohols were examined by the same technique. Alcohols studied are ethanol, *n*-propyl alcohol, isopropyl alcohol, *n*-butyl alcohol, isobutyl alcohol, *sec*-butyl alcohol and *tert*-butyl alcohol. Results obtained are summarized in Table II.

TABLE II
Chemical Species in the 1:2 Reaction System of Diethylzinc with Primary, Secondary, and Tertiary Alcohols

	Reaction temp., °C.	Primary alcohol	Secondary alcohol	Tertiary alcohol
Chemical species				
EtZnOR	30	+	+	+
	80	+	+	+
$Zn(OR)_2$	30	+	−	−
	80	+	+	−
Catalytic activity of the 1:2 system	30	+	−	−
	80	+	+	−

As can be seen in Table II, ethylzinc alkoxides, EtZnOR, are easily formed with any alcohol at 30° or 80°C. Zinc dialkoxide, $Zn(OR)_2$, was formed at 30°C. in the case of primary alcohols such as ethyl, *n*-propyl, *n*-butyl, and isobutyl alcohols, but zinc dialkoxide of secondary alcohol did not form effectively until the reaction temperature was raised to about 80°C. Reaction of diethylzinc with tertiary alcohol is most difficult, no zinc di-

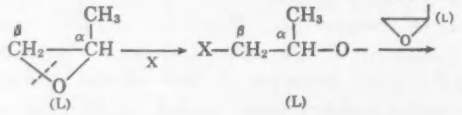
tert-butoxide being formed even at 80°C. These results also indicate the much higher velocity of reaction (1) compared to the reaction (2). Since the activity of the binary systems relates closely with the formation of zinc dialkoxide, we concluded the active species inducing the polymerization of propylene oxide to be zinc dialkoxide formed *in situ*.

Preparation of Optically Active Poly(propylene oxide) by Asymmetric Catalyst

As we reported in the previous papers,[3,4] crystalline poly(propylene oxide) prepared by diethylzinc–*d*-borneol catalyst was found to be optically active, levorotatory in benzene solution and dextrorotatory in chloroform solution. This behavior of optical rotation of the crystalline poly(propylene oxide) is similar to that of the optically active isotactic poly(propylene oxide) which was prepared by Price and his collaborators[7] polymerizing L(+)-propylene oxide with potassium hydroxide.

Since propylene oxide has an asymmetric carbon atom, there would be possible two courses for the stereoregular polymerization of racemic propylene oxide.

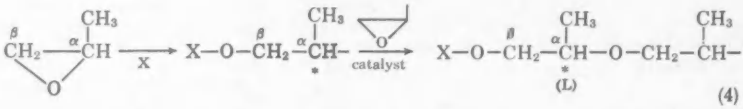
(*a*) The growing chain end selects the favorite enantiomer as reaction partner in preference over its antipode in the following way:



(3)

where the β C—O bond is broken, the configuration being retained at the α-carbon atom.

(*b*) The α C—O bond is broken, and the configuration at the starred α-carbon atom is not settled until the second monomer adds onto it as shown in eq. (4)



(4)

where the catalyst might control steric orientation of the second monomer against the growing chain end.

If eq. (3) is correct, there should be observed some optical activity in the unreacted monomer, because L- (or D-) monomer is predominantly incorporated into the polymer chain, leaving D- (or L-) monomer in excess in the unreacted monomer.

We demonstrated that this is actually the case.[4] Results of the further experiments are listed in Table III.

It can be seen from Table III that the unreacted monomer has a negative optical rotatory power. This fact shows that in the (+)-borneol–di-

TABLE III
Polymerization of Propylene Oxide by Diethylzinc–*d*-Borneol System[a]

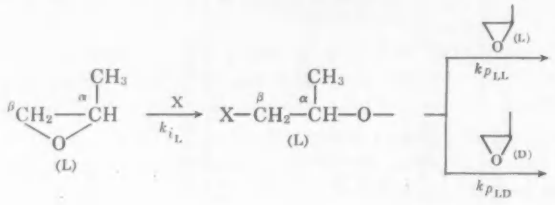
No.	Polymerization time, hr.	Conversion, %			$[\alpha]_D$		$[\eta]$	
		Crystalline	Amorphous	Total	Monomer[b]	Crystalline[c]	Crystalline[d]	Amorphous
1	5.5	0.994	0.789	1.783	−0.08	3	0.68	0.50
2	14.5	1.15	1.24	2.39	−0.24	2.5	0.20	0.38
3	23.0	3.29	8.28	11.57	−0.98	3.5	0.16	0.20
4	40.5	2.98	3.21	6.19	−0.62	2.1	0.15	0.42
5	72.0	16.1	20.8	36.9	−2.69	2.2	0.32	0.27
6	160.0	7.22	25.0	32.2	−1.28	2.8	1.06	0.76
7	48.0	4.45	13.8	18.2	−0.58	3.5	1.60	2.34
8	216.0	5.08	15.8	20.9	−1.10	4.0	0.48	0.18

[a] Reaction conditions: propylene oxide, 35 ml.; toluene 35 ml.; $ZnEt_2$, 2.4 ml.; *d*-borneol, 7.1 g.; under N_2 at 70°C.
[b] Without solvent.
[c] In chloroform.
[d] In benzene at 30°C.

ethylzinc-catalyzed polymerization L(+)-propylene oxide is consumed at a higher rate in polymerization than D(−)-monomer, and the polymer obtained should have L-monomeric unit in excess.

Mechanism of Stereospecific Polymerization of Propylene Oxide

In the polymerization of racemic propylene oxide, four propagation reactions, eqs. (5)–(8), should be considered.



(5)

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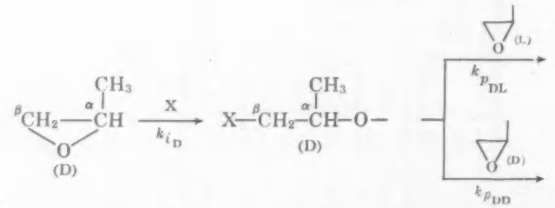


(7)

(8)

where X denotes a catalyst and k_i and k_p are the rate constants of the initiation and propagation reactions, respectively.

From the foregoing discussion, it is reasonably assumed in the isotactic polymerization that $k_{p_{LL}} > k_{p_{LD}}$ and $k_{p_{DD}} > k_{p_{DL}}$, respectively. If the catalyst X has no asymmetric centers, k_{i_L} is expected to be equal to k_{i_D}. In this case, there will be produced a mixture of polymer molecules having a certain symmetric distribution of tacticity consisting of all proportions of L- and D-monomeric units between 100% L and 100% D.

If the catalyst X carries D or L- asymmetric centers, the rate constant k_{i_L} for X_D (or X_L) should differ from k_{i_D} for X_D (or X_L). With the diethyl zinc–(+)-borneol catalyst system, k_{i_L} is larger than k_{i_D}. Therefore the polymer formed has more L-monomeric units than D- units.

The so-called stereospecific catalyst for propylene oxide polymerization is considered to have much larger $k_{p_{LL}}$ ($= k_{p_{DD}}$) than $k_{p_{LD}}$ ($= k_{p_{DL}}$).

Furthermore, results of the infrared study suggest that zinc dialkoxide formed *in situ* should rapidly convert into dimeric and trimeric forms (Fig. 4). The trimeric form is considered to be the more stable one. We interpret the catalytic activity of zinc dialkoxide in terms of the free coordination seats in monomeric and dimeric forms of the alkoxide. In other words, the driving force in the propylene oxide polymerization should be ascribed to the nature of zinc atom which exerts to stabilize its hybridization, from *sp*, via sp^2, to sp^3, by coordination.

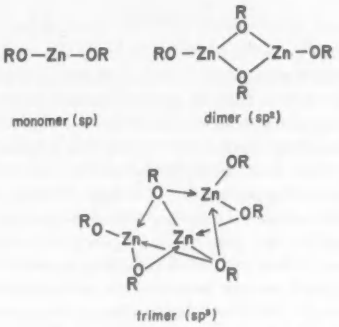
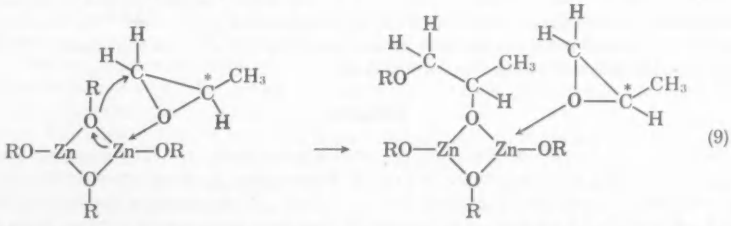


Fig. 4. Schematic structures of three types of zinc dialkoxide.

The polymerization is initiated by the coordination of propylene oxide onto the catalyst eq. (9).



(9)

In this scheme, if the catalyst has no asymmetric centers, the coordination of the first monomer is not controlled stereoselectively, but the coordination of monomers from the second on will be sterically regulated by the asymmetric center of the preceding monomer unit. Since R groups of the zinc (+)-borneolate system have asymmetric centers, every monomer entering a polymer chain could be sterically influenced by the asymmetric centers not only of the preceding monomer unit but also of bornyl groups themselves.

Further study on the tacticity of the poly(propylene oxide) prepared by asymmetric catalyst is now in progress.

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Synopsis

It was reported previously that diethylzinc induced the stereospecific polymerization of propylene oxide at room temperatures in the presence of a suitable quantity of water or alcohol. We have now found that an optically active poly(propylene oxide) can be prepared from racemic propylene oxide by use of the same kind of catalyst involving an optically active alcohol as component. For example, a mixture of 35 ml. (0.5 mole) of propylene oxide, 7.1 g. (0.046 mole) of *d*-borneol and 2.4 ml. (0.023 mole) of diethylzinc in toluene was heated under nitrogen at 80°C. for 5 hr. Polymers formed were separated into two fractions: cold acetone-soluble and acetone-insoluble fractions. The latter fraction has been identified to be crystalline poly(propylene oxide), while the soluble one is the amorphous polymer. The crystalline poly(propylene oxide) prepared in this way has been found to be optically active, levorotatory in benzene solution and dextrorotatory in chloroform solution. We have also confirmed that the unreacted monomer recovered from the reaction mixture does exhibit the levorotatory power. From these results we have concluded (+) propylene oxide to be incorporated into the polymer chain in preference to its optical antipode. On the other hand, an infrared study has indicated that the active species of the diethylzinc–alcohol system is zinc alcoholate formed *in situ*. In contrast the zinc alcoholate prepared separately, the alcoholate formed *in situ* is considered to have an *sp* or sp^2 hybridized orbital around its central zinc atom, to which the coordination of epoxide group takes place easily. On the basis of results obtained some discussion is given concerning the reaction mechanism of the stereospecific polymerization of propylene oxide.

Résumé

Comme nous l'avons publié dans les articles précédents, le diéthylzinc provoque la polymérisation stéréospécifique de l'oxyde de propylène à température de chambre en présence de quantités adéquates d'eau ou d'alcool. Nous avons maintenant montré qu'il est possible de préparer le polyoxyde de propylène optiquement actif en partant de l'oxyde du propylène racémique par le même catalyseur avec un alcool optiquement actif comme composant. On a, par exemple, chauffé une solution de 75 ml. (0.5 mole) d'oxyde de propylène, 7.1 g. (0.046 mole) du *d*-bornéol et 2.4 ml. (0.023 mole) de diéthylzinc dans le toluène sous une atmosphère d'azote à une température de 80°C. pendant 5 heures. Les polymères formés sont fractionnés en deux parties: les fractions solubles et les fractions insolubles dans l'acétone à froid. La dernière fraction est identifiée comme étant l'oxyde de polypropylène cristallin, tandis que la fraction soluble et amorphe. On montre que l'oxyde de polypropylène cristallin préparé de cette mainère est optiquement actif, lévogyre dans une solution benzénique, dextrogyre dans le chloroforme. Nous avons aussi confirmé que le monomère, qui n'a pas réagi, a un pouvoir rotatoire lévogyre. De ces résultats on a conclu que c'est l'oxyde de propylène (+) qui est incorporé de préférence dans la chaîne polymérique. D'autre part, une étude infra-rouge a indiqué que l'espèce active du système diéthyl zinc–alcool est l'alcoolate de zinc *in situ*. En opposition avec l'alcoolate préparé d'avance, l'alcoolate de zinc *in situ* est considéré comme ayant des orbitales hybrides *sp* ou sp^2 autour de l'atome central de zinc et la coordination avec les groupes époxydes se fait ainsi aisément. Sur la base de résultats acquis on accorde quelques discussions concernant le mécanisme de réaction de la polymérisation stéréospécifique de l'oxyde de propylène.

Zusammenfassung

Wie schon in früheren Arbeiten berichtet, induziert Diäthylzink die stereospecifische Polymerisation von Propylenoxyd bei Raumtemperatur in Gegenwart einer geeigneten Menge von Wasser oder Alkohol. Nun wurde gefunden, dass mit der gleichen Art Katalysator unter Verwendung einer optisch aktiven Alkoholkomponente ein optisch aktives Polypropylenoxyd aus racemischem Propylenoxyd dargestellt werden kann.

Beispielsweise wurde eine Michung von 35 ml (0,5 Mol) Propylenoxyd, 7,1 g (0,046 Mol) *d*-Borneol und 2,4 ml (0,023 Mol) Diäthylzink in Toluol unter Stickstoff durch 5 Stunden auf 80°C erhitzt. Das gebildete Polymere wurde in zwei fraktionen zerlegt, eine in kaltem Aceton löslich und die andere unlöslich. Letztere wurde als kristallines Polypropylenoxyd identifiziert, die lösliche hingegen als amorphes. Das auf diese Weise hergestellte kristalline Polypropylenoxyd erwies sich als optisch aktiv und zwar in Benzollösung linksdrehend und in Chloroformlösung rechtsdrehend. Das aus der Reaktionmischung zurückgewonnene, nicht umgesetzte Monomere zeigt Linksdrehung. Aus diesen Resultaten ist zu schliessen, dass (+) Propylenoxyd gegenüber seinem optischen Antipoden bevorzugt in die Polymerkette eingebaut wird. Andrerseits zeigte eine Infrarotuntersuchung, dass die aktive Komponente im Diäthylzink–Alkohol-System *in-situ*-Zinkalkoholat ist. Im Gegensatz zu vorgebildetem Zinkalkoholat werden dem *in-situ*-Alkoholat *sp*- oder sp^2-Hybridorbitale um das zentrale Zinkatom zugeschrieben, an welchen leicht eine Koordination der Epoxydgruppe stattfinden kann. Auf Grundlage der erzielten Ergebnisse wird eine Diskussion des Reaktionsmechanismus der Stereospezifischen Propylenoxydpolymerisation durchgeführt.

Discussion

R. E. Colclough (*Manchester University, Great Britain*): (*a*) We have studied the kinetics of the reaction between diethyl zinc and alcohol by following the gas evolution and we can confirm that the second ethyl group reacts only very slowly with alcohol at room temperature. In view of this, do the authors consider that the zinc dialkoxide is formed quantitatively in their experiments?

(*b*) The authors suggest that zinc dialkoxides are active catalysts, and exist in solution as monomeric, dimeric, and trimeric molecules. The structure proposed for the trimer would involve considerable strain, and on steric groups it seems likely that zinc alkoxides, unlike aluminium alkoxides, may only attain a coordination number of four without strain by forming an extended complex involving many molecules. We have prepared $Zn(OMe)_2$ starting from $ZnCl_2$ and LiOMe and find that the powdered crystal does not dissolve in propylene oxide, and that there is no apparent polymerization even on long standing.

We take this to indicate a high degree of intermolecular bridge-bonding which is not readily broken by propylene oxide. We have also prepared $EtZnO^iPr$ and agree that it is not an active catalyst, but we find that even this compound has a molecular complexity of approximately five in ether solution. In view of this, is there any evidence for the existence of $Zn(OR)_2$ in solution as dimeric or trimeric species?

(*c*) The question of the catalytic activity of a 2:1 mixture of alcohol and diethyl zinc might be resolved on the assumption that the active species is a soluble complex of EtZnOR and $Zn(OR)_2$ with excess alcohol as a solvating liquid, rather than the dialkoxide alone. Did the "amorphous" fraction of the polymer show any optical activity?

(*d*) From the values of the specific rotation given in Table III the rotation as measured experimentally must have been very small. What is the approximated experimental error in the values of the specific rotations quoted?

(*e*) What fraction of the polymer chains formed had a borneoxy endgroup, and was the optical activity due to these endgroups taken into account?

(*f*) In Table III the intrinsic viscosity values show a rather wide variation which seems to be independent of conversion. This is contrary to our experience with aluminium and ferric alkoxides, where the molecular weight increases with conversion. How do the authors interpret this observation, and do they consider that there is any systematic relationship between the molecular weights of the amorphous and crystalline fractions? How was the polymer fractionated?

T. Tsuruta: (*a*) The formation of dialkoxide of zinc was confirmed by the IR method and found it has close relation with the catalyst activity. If there is no $Zn(OR)_2$, the

polymerization of propylene-oxide does not take place. But the $Zn(OR)_2$ is not formed quantitatively.

(*b*) The structures for the dimer and trimer of $Zn(OR)_2$ are our speculation in reference to the Bradley theory. Colclough mentioned the lack of the catalyst activity of crystalline powder of zinc methoxide prepared from $ZnCl_2$ and $LiOCH_3$. I think the crystalline powder of the ready-made zinc methoxide has almost perfect crystal lattice where there are few active sites capable of accepting any coordination of monomer molecule.

(*c*) As I stated in my report, polypropyleneoxide is fractionated into three parts: crystalline, semi-crystalline, and amorphous (low molecular weight). Semi-crystalline fraction has the same optically active property as crystalline fraction, though the α_D value is smaller. Amorphous fraction also have come from the ending group, because the sign of α_D of the amorphous part does not change in benzene and chloroform.

(*d*) The observed values of α_D have experimental errors less than ± 0.01.

(*e*) We did no quantitative study on the endgroup, but I think one polymer chain carries one borneol group (cf., answer to Sigwalt). The infrared spectra of our polymers exhibit no absorption for bornyl group. We also examined the infrared spectra of optically inactive polypropyleneoxide plus a small quantity of borneol (or bornyl ether), and confirmed that the infrared spectra is more sensitive than our polarimetry toward the presence of bornyl group, so we concluded any correction due to bornyl group is not required in our observed α_D values of crystalline and semi-crystalline fractions.

(*f*) The method of fractionation of polypropylene-oxide was mentioned at the Symposium: crystalline (insoluble in 0°C. acetone), semi-crystalline (insoluble in −78°C. hexane), and amorphous (soluble in −78°C. hexane). Molecular weights of crystalline and semi-crystalline fractions are widely spread, and don't show any increase as the extent of polymerization increases, a fact which suggests a chain transfer reaction. We confirmed the chain transfer reaction by the use of Et_2Zn–CH_3OH system as catalyst.

R. Sigwalt (*Sorbonne, Paris, France*): Have you any information about the mean number of C^{14} atoms/macromolecule?

T. Tsuruta: We didn't study the number-average molecular weight of the produced polypropyleneoxide, so I am not sure of the mean number of C^{14} atoms/macromolecule, but I think one C^{14}/macromolecule. A sample of ours was found to have the viscosity-average molecular weight M_v., 6100. On the other hand, calculated value of number-average molecular weight, M_n, from the specific radioactivity, assuming one C^{14} atom/macromolecule, was of the polymer into consideration. The two molecular weights above mentioned are considered not to conflict with each other.

M. Farina (*Milan, Italy*): Optical rotation of polymer and of residual monomer should depend on molecular weights and on conversion.

Have you determined these relationships?

T. Tsuruta: The optically rotatory power of the polymer was found to be almost constant regardless of the difference in molecular weight and extent of polymerization, because all the polymerization experiments were interrupted in small extent of polymerization in order to obtain a polymer having the optical rotatory power as high as possible. If we continue the polymerization to larger extent, the rotatory power of the produced polymer will, of course, be decreased owing to the decrease of the concentration of L-monomer.

E. Selegny (*Faculté de Nantes, France*): Have you any x-ray diffraction data on your polymer, and which is the tacticity?

T. Tsuruta: The x-ray diffraction pattern of our optically active polymer was found to be much the same as that of the optically inactive crystalline polypropylene oxide. This should be anticipated from the fact that even Price's isotactic polymer of L-propylene oxide did exhibit the same crystalline x-ray pattern as the usual crystalline polypropyleneoxide.

The tacticity of our optically active polymer was found at least 72% of L-unit from

the value of optical rotation. I believe the polymer molecule to have a "block" type enchainment such as ~LLLL...LDD...DLL....L~.

K. Wilkinson (*Milan, Italy*): In your mechanism (eq. 9) would you not expect relatively rapid exchange between the positions of all the optically active alkoxide groups and the growing chain position, and hence growth on all the alkoxide groups, so that all the (+)-borneoxy groups become chain endgroups? If this is so why do you find no decrease in optical specificity of the catalyst and hence α_D for the polymer with increasing conversion?

T. Tsuruta: Such an exchange reaction may be possible, so I think we must examine it by suitable experiments.

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Mechanism of Stereoregular Polymerization of Acetaldehyde

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It is known that acetaldehyde is polymerized to isotactic polymer by aluminum trialkyl and alkoxide catalysts.[1–3] The real active species of the stereoregular polymerization of acetaldehyde with trialkylaluminum catalyst has been reasonably assumed to be aluminum alkoxide having the general formula, $R_{3-n}Al(OR')_n$ (n = 1, 2, or 3), but the stereospecificity of trialkylaluminum is much lower than that of aluminum alkoxide itself. Therefore, it may be suggested that the nature of the ligand of aluminum will have an influential effect on the stereospecificity of the catalyst.

In this study, we carried out a series of experiments of acetaldehyde polymerization in which diethylaluminum alkoxides, $(C_2H_5)_2AlOR$, of various alkoxy groups were employed as the catalyst, and found that the bulkiness of alkoxy group was closely related to the stereospecificity of the catalyst. The bulkier the alkoxy group was, the higher the stereospecificity of the catalyst became. For increasing stereospecificity, the effect of the branching degree at the α-carbon atom of the alkoxy group prevails over that of its length.

EXPERIMENTAL

Material

Acetaldehyde. Commercial paraldehyde was treated successively with sodium carbonate and sodium sulfate and then rectified over calcium hydride (b.p. 122–122.5°C.). The pure paraldehyde thus obtained was decomposed into acetaldehyde by anhydrous copper sulfate under nitrogen atmosphere. Crude acetaldehyde was fractionated over calcium hydride through a water-cooled column, b.p. 20.6–20.8°C.

Triethylaluminum. A commercial sample was distilled under nitrogen, b.p. 66–67°C./3 mm. Hg.

Alcohols. Commercial reagents of the highest purity were dried by usual methods and distilled.

Solvents. Commercial reagents of pure grade were dried and distilled.

Preparation of Catalytic System

The diethylaluminum alkoxide catalysts were prepared by the reaction between equimolar amounts of triethylaluminum and various alcohols:

$$(C_2H_5)_3Al + ROH \rightarrow (C_2H_5)_2AlOR + C_2H_6 \uparrow$$

In a round-bottomed flask was placed a solution of 0.34 ml. (0.0025 mole) of triethylaluminum in 20 ml. of *n*-hexane under nitrogen atmosphere. When 0.0025 mole alcohol was added at room temperature, an exothermic reaction occurred immediately. The mixture was left at room temperature for half an hour.

The completion of the reaction was examined as follows. The reaction mixture was subjected to vacuum distillation first at room temperature and later at 50°C. The distillate was collected in a trap immersed in a Dry Ice–alcohol bath. The content of the unreacted alcohol was analyzed by gas chromatography. The reliability of this analytic procedure had been confirmed by a reference run in which the calculated amount of isopropyl alcohol was recovered from its mixture with aluminum isopropoxide.

TABLE I
Reaction of Triethylaluminum and Alcohol[a]

Alcohol	Reaction temperature	Unreacted alcohol, mole[b]	Extent of reaction, %
C_2H_5OH	Room temp.	0	100
n-C_3H_7OH	Room temp.	0	100
i-C_3H_7OH	Room temp.	0.18×10^{-3}	93
i-C_3H_7OH	98°C., 1 hr.	0	100
n-C_4H_9OH[c]	Room temp.	0	100
i-C_4H_9OH	Room temp.	0	100
sec-C_4H_9OH	Room temp.	0[d]	100
tert-C_4H_9OH	Room temp.	0	100

[a] Reaction conditions: $Al(C_2H_5)_3$ and alcohol, each 2.5 times 10^{-3} mole; *n*-heptane, 20 ml.; reaction for 1/2 hr.

[b] Unreacted alcohol was determined by gas chromatography.

[c] Reaction was carried out in *n*-hexane.

[d] A trace of alcohol was recovered.

Table I shows that most alcohols except isopropyl alcohol react completely with an equimolar amount of triethylaluminum under the experimental conditions. The reaction between equimolar amounts of isopropyl alcohol and triethylaluminum was found to be completed by heating at the boiling point of *n*-heptane for 1 hr.

Polymerization Apparatus and Method

The apparatus for polymerization is shown in Figure 1; it is similar to that employed in the acetaldehyde polymerization with alumina catalyst.[4]

Under nitrogen atmosphere, 20 ml. of catalyst in hexane solution was placed in flask B and 15 ml. of the acetaldehyde monomer in the flask A.

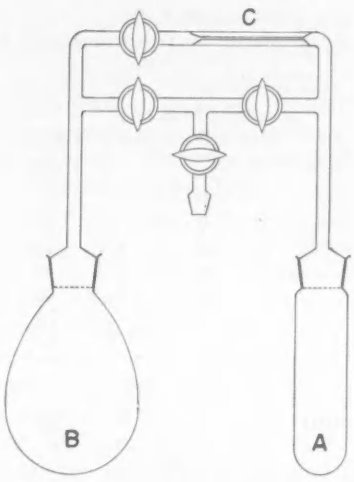


Fig. 1. Polymerization apparatus.

Both A and B were cooled with Dry Ice–alcohol baths, and the whole system was evacuated to 1–2 mm. Hg. Then, the Dry Ice Bath of A was removed and the monomer was allowed to distill into B through the capillary C at a rate of about one-sixth mole of monomer per hour. After all the monomer had been added to the catalyst solution, the reaction mixture was kept at −78°C. for 44 hr. Then, about 100 ml. of methanol containing a small amount of pyridine was added to the reaction mixture. The polymeric product was obtained as white mass, which was extracted with methanol and separated into two fractions; i.e., methanol-soluble and methanol-insoluble fractions. The methanol-soluble fraction was recovered by reprecipitation in large excess of water. Both fractions were dried *in vacuo* at room temperature.

X-Ray Diffraction by Geiger Counter

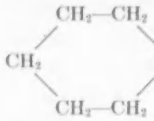
Crystallinities of the methanol-insoluble fractions prepared with various catalyst species of $(C_2H_5)_2AlOR$ were compared by x-ray Geiger counter spectra which were taken with film specimens of the same thickness. The thickness of the films was adjusted by repeated calendering on a roll, the average thickness being 0.237 mm.

RESULTS AND DISCUSSION

The results of polymerization with $(C_2H_5)_2AlOR$ catalysts are summarized in Table II.

It is known that the solubility of high polymer of acetaldehyde is decisively controlled by its stereoregularity, i.e., atactic polymer is always soluble in common organic solvents including methanol even if its molecular

TABLE II
Polymerization of Acetaldehyde by Triethylaluminum–Alcohol Systems[a]

Alcohol	Degree of branching at α-carbon atom	Polymer	
		Yield, %	Insoluble fraction, %[b]
None[c]	—	39	15
CH_3CH_2OH	0	36	14
$CH_3(CH_2)_5OH$	0	59	22
$CH_3(CH_2)_6OH$	0	45	22
$CH_3(CH_2)_7OH$	0	44	34
$(CH_3)_2CHCH_2OH$	0	35	29
$(CH_3)_2CHOH$	1	75	73
$CH_3CH_2CH(CH_3)OH$	1	62	79
	1	29	45
$(CH_3)_3COH$	2	14	86

[a] Reaction conditions: CH_3CHO, 0.25 mole; $Al(C_2H_5)_3$ and alcohol, each 0.0025 mole; *n*-hexane, 20 ml.; polymerization at −78°C. for 44 hr.

[b] Percentage of the methanol-insoluble fraction based on the total polymer.

[c] Polymerization by $Al(C_2H_5)_3$ alone.

weight is extremely high.[4] Therefore the relative amount of the methanol-insoluble fraction may be taken as a measure of stereoregularity of the product polymer. Table II indicates that the bulk of alkoxy group affects the stereospecificity of the $(C_2H_5)_2AlOR$ catalyst. Here it is to be noted that the degree of branching at the α-carbon atom of the alkoxy group is more effective for increasing stereospecificity than the length, e.g., $(C_2H_5)_2$-$(CH_2)_7CH_3$ is less stereospecific than $(C_2H_5)_2AlOCH(CH_3)_2$. Moreover,

TABLE III
X-Ray Crystallinities of Methanol-Insoluble Fractions Prepared by Triethylaluminum–Alcohol System (Film Thickness 0.237 mm.)

Alcohol	Integrated intensity cm.[2a]	Relative intensity[b]
$(CH_3)_3COH$	16.16	100
$CH_3CH_2CH(CH_3)OH$	9.46	59
$(CH_3)_2CHOH$	7.38	46
$CH_3(CH_2)_7OH$	4.39	27
None[c]	0	0

[a] Area under the peak at $2\theta = 12°12'$ (200).

[b] Relative intensity was calculated on the basis that the intensity of the insoluble fraction prepared by $(C_2H_5)_2AlOC(CH_3)_3$ was 100 and that of amorphous polymer by alumina catalyst was zero.

[c] Amorphous polymer was prepared by alumina catalyst.

branching at the β-carbon atom is much less influential than that at the α-carbon atom. The higher the degree of branching at α-carbon of alkoxy group is, the more stereospecific the catalyst becomes.

Besides the relative amount of the insoluble fraction of the product polymer, the x-ray crystallinity of the insoluble fraction can be another index of the stereospecificity of catalyst. The x-ray crystallinity was estimated by the integrated intensity determined by the area under the peak at $2\theta = 12°12'$ of the Geiger counter spectrum. The results are shown in Table III.

In Table III, only for the sake of comparison, the relative intensity was tentatively calculated on the basis that the intensity of the insoluble fraction prepared by $(C_2H_5)_2AlOC(CH_3)_3$ was 100 and that of amorphous polymer by alumina catalyst was zero.

The order of stereospecificity of the catalyst determined by the x-ray crystallinity of the product polymer agrees with that given by the relative amount of insoluble fraction of the total polymer.

From these results it can be concluded that the stereospecificity of the catalyst $(C_2H_5)_2AlOR$ for the acetaldehyde polymerization increases with the bulk of the alkoxy group, the degree of branching at the α-carbon atom being more influential than the length. This conclusion seems to suggest that the steric control in the propagation step is afforded by the steric hindrance of the alkoxy ligands bound to the propagation center.

The polymerization reaction of acetaldehyde is closely related to the Meerwein-Ponndorf reduction. The relation between these two reactions has been discussed,[3] and the coordination of carbonyl group to aluminum alkoxide which was detected by the shift of the carbonyl band of the infrared spectrum was illustrated as one of the features common to both of them.[5] The steric control by alkoxy group in the stereospecific polymerization seems to correspond to the asymmetric reduction of carbonyl compound with aluminum alkoxide consisting of optically active alkoxy group.[6,7]

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Synopsis

It is known that aluminum trialkyls and aluminum alkoxides are stereoregular catalysts for the polymerization of acetaldehyde to isotactic polymer. Although the active species of the trialkylaluminum catalyst has been considered to be alkylaluminum alkoxide, $R_{3-n}Al(OR')_n$ ($n = 1$ or 2), aluminum trialkyl and aluminum alkoxide are different from each other in stereoselectivity. Usually, the stereospecificity is estimated by

two ways: fractionation with a set of extraction solvents and the measurement of tacticity of each fraction. We carried out the acetaldehyde polymerization by using $(C_2H_5)_2$-AlOR catalytic systems which were derived from the reactions of equimolar amounts of triethylaluminum and various alcohols. After polymerization, the polymeric product was separated by methanol extraction into amorphous (methanol-soluble) and crystalline (methanol-insoluble) fractions. The crystallinity of the methanol-insoluble fraction was estimated from the area under the first peak at $2\theta = 12°12'$ of the x-ray Geiger spectrum. The orders of stereoselectivity of $(C_2H_5)_2AlOR$ species estimated by these two methods agreed with each other. The diethylaluminum alkoxide species containing ethoxy, *n*-propoxy, *n*-butoxy, isobutoxy and *n*-octyloxy groups were lower in stereospecificity than those having isopropoxy and *sec*-butoxy groups. The stereospecificity of diethylaluminum *tert*-butoxide was the highest. It is thus concluded that the alkoxyl group of $(C_2H_5)_2AlOR$ much affects the stereospecificity and that the degree of branching at the α-carbon atom of the alkoxyl group is more influential than the length of the alkoxyl group.

Résumé

On sait que le trialcoylaluminium et l'alcoxyde d'aluminium sont des catalyseurs stéréoréguliers pour la polymérisation de l'acétaldéhyde en donnant un polymère isotactique. Quoique l'on considère comme étant l'espèce active du catalyseur trialcoylaluminium, l'alcoxyde d'aluminium $R_{3-n}Al(OR)_n$ ($n = 1$ ou 2), le trialcoylaluminium et l'alcoxyde d'aluminium sont différents l'un de l'autre du point de vue de la stéréosélectivité. On évalue habituellement la stéréospécificité de deux manières: par fractionnement au moyen d'un procédé d'extraction par solvants et par la mesure de la tacticité de chaque fraction. Nous avons polymérisé l'acétaldéhyde au moyen du système catalytique $(C_2H_5)_2AlOR$, provenant de la réaction de quantités équimoléculaires de triéthylaluminium et de différents alcools. Après la polymérisation, on sépare le polymère par extraction au méthanol en fractions amorphes (solubles dans le méthanol) et en fractions cristallines (insolubles dans le méthanol). On évalue la fraction insoluble dans le méthanol à partir des surfaces comprises dans le premier pic à $2\theta = 12°12'$ du spectre de rayons-X Geiger. Les ordres de stéréosélectivité des espèces $(C_2H_5)_2AlOR$ estimées par ces deux méthodes s'accordent. Les espèces d'alcoxyde de diéthylaluminium contenant les groupes éthoxy, *n*-propoxy, *n*-butoxy, *i*-butoxy et *n*-octyloxy ont un pouvoir stéréospécifique plus faible que ceux ayant les groupes *i*-propoxy et *sec*-butoxy. La stéréospecificité du *t*-butoxyde de diéthylaluminium est la plus élevée. On conclut donc que le groupe alcoxyde $(C_2H_5)_2AlOR$ affecte beaucoup la stéréospécificité et que le degré de ramification de l'atome de carbone-alpha du groupe alcoxyde a plus d'influence que la longuer du groupe alcoxyle.

Zusammenfassung

Es ist bekannt, dass Trialkylaluminium und Aluminiumalkoxyd stereospezifische Katalysatoren für die Polymerisation des Acetaldehyds zu isotaktischen Polymeren sind. Obgleich als aktive Komponente des Trialkylaluminiumkatalysators Alkylaluminiumalkoxyd, $R_{3-n}Al(OR)_n$ ($n = 1$ oder 2), in Betracht gezogen wurde, unterscheiden sich Trialkylaluminium und Aluminiumalkoxyd doch in ihrer Stereoselektivität. Üblicherweise wird die Stereospezifität durch zwei Messungen bestimmt: Fraktionierung mit einer Reihe von Extraktionslösungsmitteln und Bestimmung der Taktizität jeder Fraktion. Wir führten die Acetaldehydpolymerisation mit Katalysatorsystemen, $(C_2H_5)_2AlOR$, aus äquimolaren Mengen von Triäthylaluminium und verscheidenen Alkoholen durch. Nach der Polymerisation wurde das polymere Produkt durch Methanolextraktion in eine amorphe (Methanol-lösliche) und eine kristalline (Methanol-unlösliche) Fraktion zerlegt. Die Kristallinität der methanolunlöslichen Fraktion wurde aus der Fläche unter dem ersten Maximum bei $2\theta = 12°12'$ des Röntgen-Geigerspektrums bestimmt. Die nach diesen beiden Methoden bestimmte Reihen-

folge der Stereoselektivität der $(C_2H_5)_2AlOR$-Verbindungen war die gleiche. Diäthylaluminium-alkoxydverbindungen mit Äthoxy-, *m*-Propoxy-, *n*-Butoxy, *i*-Butoxy- und *n*-Octyloxygruppen besassen eine niedrigere Stereospezifität als solche mit *i*-Propoxy und *sek*-Butoxygruppen. Die höchste Stereospezifität besass Diäthylaluminium-*t*-butyoxyd. Man kommt zu dem Schluss, dass die Alkoxylgruppe von $(C_2H_5)_2AlOR$ einen grossen Einfluss auf die Stereospecifität besitzt und dass der Grad der Verzweigung am α-Kohlenstoffatom der Alkoxylgruppe wichtiger ist als die Länge der Alkoxylgruppe.

Discussion

R. O. Colclough (*Manchester University, Great Britain*): (*a*) If both the ethyl groups and the alkoxy group remain attached to the metal atom during propagation, the active center must be cationic. If, on the other hand, the alkoxy group is initially transferred to the polymer chain and removed from the vicinity of the metal atom, it is difficult to see how it could affect stereoselectivity during propagation. Is there any evidence as to the estimated fate of the alkoxy groups originally attached to the metal?

(*b*) Tsuruta et al. ascribe the stereoselective influence in propylene oxide polymerization to the groups which remain attached to the metal atom throughout the propagation process. This cannot apply to the variation found in the present system, since the remaining groups are ethyl in all the catalysts used. Are any of these groups displaced, and if not, how is the stereoselective process envisaged?

(*c*) It is clearly of great importance to determine as precisely as possible the constitution of the catalyst both before and after polymerization. We are at present investigating the reaction between metal alkyls and alcohols, and preliminary results show that a 1:1 molar ratio of $Al(Me)_3$ to alcohol necessarily gives a single product in solution. If we take a change in reactivity towards excess alcohol as a criterium of compound formation, the reaction of $Al(Me)_3$ with ethanol in hexane solution at 0°C. shows definite changes in rate at molar ratios $[EtOH]/[AlMe_3]$ of 0.5:1 and 1.67:1, but not at 1:1, although the methane evolution and molecular weight at the 1:1 ratio correspond to the formation of $[(Me)_2AlOEt]_2$.

J. Furukawa: There may be two possible explanations to the fact that the OR group of Et_2AlOR catalyst affects the stereospecificity of this catalyst. The first is that the ethyl anion initiates the polymerization. The second is that the initiation is by OR anion of the associated complex of catalyst consisting of two or more molecules of Et_2AlOR species. At present, we prefer the second possibility to the first. In the associated complex of $(Et_2AlOR)_n$, OR groups remain in the vicinity of the active site to effectuate stereoregulation. The fate of OR group is now being examined in detail.

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Crystalline Hydrocarbon Polymers by Cationic Hydride Shift Mechanism

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I. INTRODUCTION

Relatively high molecular weight, rubbery, soluble polymers of unknown structure were first obtained from 3-methylbutene-1 in our laboratories more than 20 years ago by cationic polymerization with aluminum chloride–ethyl chloride catalyst solution at −78°C.[1] Fifteen years later, Natta and co-workers disclosed the polymerization of this same monomer at room temperature with metal alkyl coordination catalysts to give a crystalline, high melting, insoluble polymer having a conventional 1,2 head-to-tail isotactic structure.[2] Finally, in 1960, we showed that a third polymeric form of 3-methylbutene-1 could be made by cationic polymerization with aluminum chloride–ethyl chloride catalyst by decreasing the temperature of reaction to −130°C.[3] This was done with knowledge that a lowering of the temperature would favor the formation of a syndiotactic polymer. The resulting product, a white, crystalline powder of low melting point (~ 55°C.) and soluble character, gave an x-ray diffraction pattern significantly different from that of isotactic poly-3-methylbutene-1 and was first thought to be syndiotactic. However, NMR data indicated an unusual α,α'-dimethylpropane repeat unit which in turn suggested a 1,3-intramolecular hydride shift polymerization mechanism. Because of the potential significance of this indication, additional work to clarify the structure of the cationic polymerization products has been undertaken as reported here.

II. EXPERIMENTAL

1. Polymer Synthesis

General polymerization technique has been reported.[4] Rubbery, amorphous, cationic poly-3-methylbutene-1 was obtained with aluminum chloride catalyst at −78 to −98°C. The crystalline cationic polymer was prepared at −130°C. The isotactic product was synthetized with an aluminum alkyl transition metal halide complex catalyst. A soluble reference sample for spectroscopic investigations has been prepared by our

associate Dr. H. F. Strohmayer through hydrogenation of poly-3,4-isoprene. This material is expected to have the same basic structure as that of head-to-tail poly-3-methylbutene-1. The poly-3,4-isoprene was obtained according to the procedure of Wilke.[5]

2. Vacuum Pyrolysis

High vacuum pyrolysis of various poly-3-methylbutene-1 samples and the hydrogenated poly-3,4-isoprene was carried out at two levels of cracking severity as follows.[6]

Depolymerization Procedure A. Samples of 1.0 g. were depolymerized in an all-glass apparatus consisting of a short-necked flask, heated in a Wood's metal bath, and sealed to traps for the isolation and collection of viscous oil products, more volatile liquid fractions and, finally, gases. The samples were pumped off until melted (ca. 230°C.), the system was closed off, and wet-ice and liquid nitrogen traps put in place. The samples were heated in a controlled cycle of 50 min. to 490°C., followed by 10 min. at 490°C. With the short path still used, over 95% of the charge distilled out and 70–80% of it was retained as a viscous oil in the wet-ice trap. The heavy oil and light oil fractions were then degassed and the total gas sample collected in the third and last trap over mercury.

Depolymerization Procedure B. This procedure was the same as that of procedure A above except that a 0.5-g. sample was used; the still-pot had a long neck which resulted in refluxing of the sample; and a different temperature cycle was employed, viz., 6 min. at 410°C., 20 min. at 420–440°C., 10 min. at 480°C., and 10 min. at 505°C.

In general, three samples were collected which taken together represented at least 80% of the polymers charged. The gas samples (C_1–C_5) representing 4.4–16.5% of charge were assayed by gas chromatography using a 2,5-hexenedione column. The light oil fractions (C_6–C_{10}), representing about 20% of charge, were collected in a liquid nitrogen trap, degassed at room temperature and pressure, and analyzed by infrared spectroscopy. The heavy oil fractions, representing about 40% of charge, were collected in a wet-ice trap, degassed at 100°C. and atmospheric pressure, and then analyzed by infrared technique.

3. Spectroscopic Techniques

X-ray diffraction, infrared, and nuclear magnetic resonance spectra of various poly-3-methylbutene-1 samples and hydrogenated poly-3,4-isoprene were investigated.

III. RESULTS AND DISCUSSION

1. NMR Investigations

The NMR spectra of polyisobutylene and cationic poly-3-methylbutene-1 are quite similar. Both spectra show only two distinct peaks,

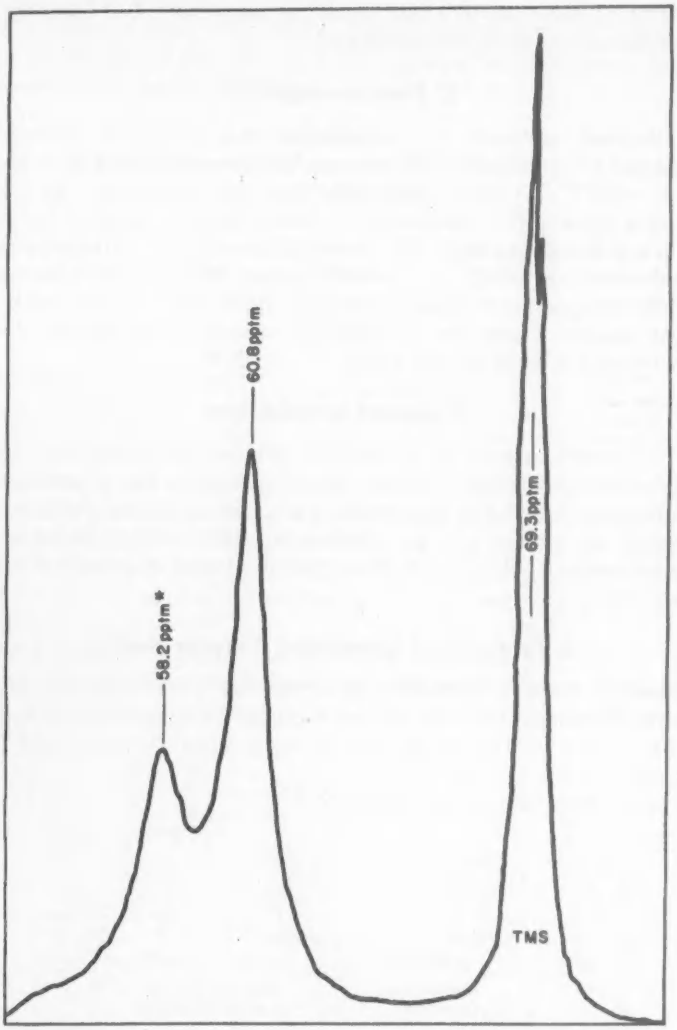


Fig. 1. NMR spectrum (60 Mcycles/sec.) of cationic poly-3-methylbutene-1.

one which is characteristic of the methylene and the other of the methyl hydrogens. Significantly, the area ratio of these peaks of the cationically obtained crystalline poly-3-methylbutene-1 is 1.5 indicating 6-methyl and 4-methylene hydrogens (Fig. 1). Cationic samples obtained at higher working temperatures exhibited higher area ratios, indicating that they were mixtures of the proposed 1,3 structure and the conventional 1,2 structure. The tertiary hydrogens are not completely resolved in present

day NMR spectra, so that this technique cannot be relied upon for the quantitative analysis of these mixtures.

2. X-ray Investigations

Cationically obtained poly-3-methylbutene-1 exhibits a distinctively crystalline x-ray diffraction pattern provided the polymerization is carried out at $-130°C$.[3] Careful examination of a large number of x-ray diffraction data revealed the existence of two distinct types of patterns, which we call α and β modifications. The repeat distance in the c direction of an α sample was found to be 7.8 A. in oriented films. This figure is in agreement with the proposed α,α'-dimethylpropane repeat unit. Consequently the repeat distance of the low temperature cationic poly-3-methylbutene-1 would consist of two structural units.[7]

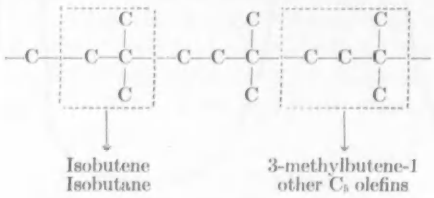
3. Infrared Investigations

The infrared spectra of cationically obtained poly-3-methylbutene-1 samples were compared to those of (solubilized) isotactic samples and hydrogenated poly-3,4-isoprene specimens. The spectra of the latter two polymers are similar and are significantly different from those of the cationic product. The results of a detailed infrared investigation will be published.[6]

4. Pyrolysis and Quantitative Structure Studies

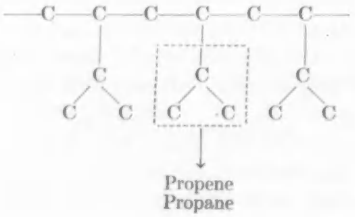
Gaseous Fraction Obtained by Pyrolysis. Observations regarding analysis of gaseous fractions derived from the two types of polymers investigated are interpreted in light of the proposed structures and products shown in eqs. (1) and (2):

Product from cationic polymerization:



(1)

Product from metal alkyl coordination catalyst:



(2)

An examination of data summarized in Table I shows results in accord with these expectations. The data in Table I include estimated percentages of 1,2 polymer in the rubbery cationic polymerization products, using the isotactic polymers as reference.

TABLE I
Composition of the Gaseous Fractions of Pyrolyzed Poly-3-methylbutene-1 Samples in Mole-% Selected Values

	Cationic, (avg. of 3)	Isotactic, (avg. of 2)	Hydrogenated poly-3,4-isoprene	Maximum 1,2 in cationic polymer, (estimated)
Propane	11.1	61.8	59.0	18
Isobutene	26.3	6.7	5.3	
Total saturates	23.8	65.6	67.2	35.4
				26.7

The close match in composition between the reference polymer gas decomposition products and those of products from hydrogenated poly(3,4-isoprene) is remarkable. These results lead us to conclude that the cationic polymers of 3-methylbutene-1 are not formed exclusively by 1,3 polymerization, but are mixtures of some description of the 1,3 and 1,2 type polymer structures.

Liquid Fractions. Infrared analysis of the liquid fractions obtained by high vacuum pyrolysis confirm the conclusion reached from chromatographic examination of gaseous fractions. Salient results are summarized in Table II.

TABLE II
Summarized Infrared Results

Olefin types	Formulae	Cationic poly-3-methyl-butene-1	Isotactic poly-3-methyl-butene-1	Hydrogenated poly-3,4 isoprene
I	$CH_2{=}CH{-}$	Very strong	Very weak	Very weak
IIt	*trans*-$CH{=}CH{-}$	Weak	Medium	Medium
III	$CH_2{=}\overset{CH_3}{\overset{|}{C}}{-}$	Weak	Very strong	Very strong

From a study of the proposed structures it is apparent that vinyl endgroups (Type I olefins) are obtained from the 1,3 (cationic) structure, whereas $CH_2{=}CCH_3{-}$ (Type II olefins) endgroups are formed from the 1,2 (conventional) skeleton on pyrolysis. And in fact this is what has been found as shown in Table II.

Minor amounts of type IIt olefins are found in all the polymer decomposition products. Their peak intensities vary directionally with those of the

type III olefins. They are attributed to the 1,2 type polymers and are believed to come from isomerization of type III olefin structures. This explanation is supported by calculated estimates of 1,2 polymer structure in cationic poly-3-methylbutene-1, assuming that the isotactic polymer is 100% 1,2 structure. These estimates are given in Table III.

TABLE III
Estimated 1,2 Structure Content of Poly-3-Methylbutene-1 Samples Based on Infrared Examination of Liquid Fraction Obtained by Pyrolysis

	1,2 Content, %	
	Infrared band (type III) $CH_2=\overset{CH_3}{\overset{|}{C}}-$	Infrared band (type IIt) —CH=CH—
Cationic product 1	41.5	25.2
Cationic product 2	39.9	27.6

These infrared interpretations of the structure of cationic polymerization products are in reasonable agreement with independent conclusions reached from chromatographic examinations of gaseous fractions and therefore, support the view that the cationic polymerization products made at −98°C. are mixtures of about 30% of a 1,2 structure and about 70% of a 1,3 structure. This finding provides tangible evidence for the intramolecular 3,2 hydride shift polymerization reaction mechanisms postulated earlier.[3] In view of its scientific interest, the work is to be continued further.

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Synopsis

The low temperature cationic polymerization of 3-methylbutene-1 has been investigated. A crystalline high polymer was obtained with either aluminum chloride, aluminum bromide, or titanium tetrachloride catalysts in ethyl chloride diluent at −130°C. This is the first case of a cationic synthesis of a crystalline aliphatic α-polyolefin. At temperatures higher than −130°C. only amorphous polymers were obtained. The physical properties of the crystalline polymer modification are reported. X-ray diffraction and other studies demonstrated that the crystalline poly-3-methylbutene-1 is not an isotactic material. Nuclear magnetic spectra indicate that this polymer has an unusual α,α'-dimethylpropane $+CH_2CH_2C(CH_3)_2+$ repeating unit. The

mechanism of the polymerization involves initiation, e.g., protonation of the monomer and the formation of a secondary carbonium ion, isomerization, e.g., formation of an energetically favored tertiary carbonium ion by a 3→2 hydride shift, and propagation, e.g., attack of the tertiary carbonium ion on a monomer molecule. The structure of this novel polymer has been investigated by comparisons with well-defined compounds. Thus isotactic poly-3-methylbutene-1 and cationic poly-3-methylbutene-1 were heat degraded. Whereas the isotactic polymer yielded large amounts of C_3 fragments (pendant isopropyl groups) and very little C_4 fragments, the cationic material yielded much less C_3 fragments but gave an appreciable C_4 fraction. In similar structure studies isoprene was polymerized to 3,4 enchainment by a Ziegler-Wilke catalyst and the product hydrogenated. This product (a bonafide head-to-tail polymer of 3-methylbutene-1) was significantly different from the cationically obtained high polymer.

Résumé

On a étudié la polymérisation cationique du 3-méthylbutène-1 à basse température. On a obtenu un polymère hautement cristallin avec des catalyseurs soit de chlorure d'aluminium, de bromure d'aluminium ou de tétrachlorure de titane dans le chlorure d'éthyle comme diluant à −130°C. Ceci est le premier cas de synthèse cationique d'une aliphatique alpha-polyolefine cristalline. A des températures supérieures à −130°C on a obtenu seulement de polymères amorphes. On rapporte les propriétés physiques de la modification du polymère cristallin. La diffraction des rayons-X et d'autres études montrent que la poly 3-methylbutène-1 n'est pas une substance isotactique. Les spectres de résonance magnétique nucléaire montre que ce polymère présente la répétition d'une unité α,α'-dimethylpropane non-habituelle $+CH_2CH_2C(CH_3)_2+$. Le mécanisme de polymérisation comprend l'initiation à savoir protonation du monomère et formation d'un ion carbonium secondaire, l'isomération à savoir la formation par glissement d'hydrure 3→2 d'un ion carbonium tertiaire énergétiquement favorisé, et la propagation à savoir d'attaque d'une molécule de monomère par l'ion carbonium tertiaire. L'etude de la structure de ce nouveau polymère a été faite par comparaison avec des composés bien définis. Le poly 3-méthylbutène-1 isotactique et le poly-3-méthylbutène-1 cationique ont été dégradés thermiquement. Alors que le polymère isotactique fournit de grandes quantités de fragments en C_3 (groupements isopropyles pendants) et très peu de fragments C_4, le polymère cationique fournit beaucoup moins de fragments en C_3 mais a donné une fraction en C_4 appreciable. Dans des études de structures similaires, de l'isoprène a été polymérisé en enchaînement 3,4 par un catalyseur de Ziegler-Wilke et le produit a été hydrogéné. Ce produit (un polymère du 3-méthylbutène-1 à structure tête-à-queue) différait significativement du haut polymère obtenu cationiquement.

Zusammenfassung

Die kationische Tieftemperaturpolymerisation von 3-Methylbuten-1 wurde untersucht. Mit Aluminiumchlorid, Aluminiumbromid oder Titantetrachlorid als Katalysator wurde in Äthylchloridlösung bei −130°C ein kristallines Hochpolymeres erhalten. Es ist das der erste Fall einer kationischen Synthese eines kristallinen Polyolefins. Bei höheren Temperaturen als −130° wurden nur amorphe Polymere erhalten. Die physikalischen Eigenschaften der kristallinen Polymermodifikation werden mitgeteilt. Röntgenbeugung und andere Untersuchungen zeigten, dass das kristalline Poly-3-methylbuten-1 keine isotaktische Substanz ist. Kernmagnetische Resonanzspektren lassen erkennen, dass dieses Polymere einen ungewöhnlichen α,α'-Dimethylpropan-Baustein, $+CH_2CH_2C(CH_3)_2+$, besitzt. Der Polymerisationsmechanismus besteht aus einer Startreaktion, z.B. Protonierung des Monomeren und Bildung eines sekundären Carboniumions, Isomerisierung, z.B. Bildung eines energetische begünstigten tertiären Carboniumions durch eine 3→2-Hydridverschiebung und Wachstum, z.B. Angriff des tertiären Carboniumions an ein Monomermolekül. Zur Untersuchung der Struktur

dieses neuartigen Polymeren wurde ein Vergleich mit gut definierten Verbindungen durchgefühft. So wurde ein thermischer Abbau von isotaktischem Poly-3-methylbuten-1 und kationischem Poly-3-methylbuten-1 durchgeführt. Während isotaktische Polymere gross Mengen von C_5-Bruchstücken (Isopropylseitengruppen) und sehr wenig C_4-Bruchstücke lieferte, ergab die kationische Substanz viel weniger C_5-Bruchstücke aber eine beträchtliche C_4-Fraktion. Zu einem weiteren Strukturvergleich wurde Isopren mit einem Ziegler-Wilke-Katalysator in ein 3,4-Polymeres umgewandelt und das Reaktionsprodukt hydriert. Diese Substanz (als Kopf-Schwanz-Polymeres von 3-Methylbuten-1 zu betrachten) unterschied sich deutlich von dem kationisch erhaltenen Hochpolymeren.

Discussion

Dr. Eroussalimsky (*Léningrad, U.S.S.R.*): It would be very interesting to have some features of the kinetics of the process you have studied. In the well known fundamental studies of the cationic polymerization of Mr. R. M. Thomas and Dr. J. P. Kennedy was found a phenomenon of inversion temperature, that is of unusual dependencies of $\bar{M}$ on the monomer concentration. I should like to inquire if something similar could be found in the case of 3-methyl-butene-1. Was something analogous observed?

R. M. Thomas: The kinetics of this polymerization system has been investigated and the results are to be published soon in *J. Polymer Science* Evidence for the existence of an inversion temperature was not encountered.

N. A. Plate (*Moscow, U.R.S.S.*): What do you think about the possibility of realizing such a hydride-ion shift in the case of hydrogen atom from CH_3-group?

R. M. Thomas: We consider such a shift to be highly unlikely as it would require the transformation of a secondary carbonium ion to a primary carbonium ion.

N. A. Plate: How about the influence of additional CH_2-group in efficiency of hydride shift, like in the case of 4-methylpentene?

R. M. Thomas: Hydride shift occurs in the cationic polymerization of 4-methyl-1-pentene as reported by Edwards and Chamberlain at the 142nd meeting of the ACS, Atlantic City, September 1962. The situation is more complicated than that of 3-methyl-1-butene and it is still under investigation in our laboratories.

MECHANISM AND KINETICS OF STEREOSPECIFIC POLYMERIZATIONS IN HOMOGENEOUS MEDIA

JOURNAL OF POLYMER SCIENCE: PART C NO. 4, PP. 299–309

Sur le Mécanisme d'une Polymérisation Anionique du Chlorure de Vinyle

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Dans une récente publication,[1] nous avons décrit la préparation d'un polychlorure de vinyle (PVC) cristallin, partiellement insoluble à froid, mais de faible poids moléculaire. Cette préparation était effectuée par polymérisation anionique en milieu tétrahydrofurane (THF), catalysée par une solution filtrée de chlorure de tertiobutyle-magnésium. L'analyse chimique centésimale et la spectrographie infra-rouge nous ont permis d'attribuer à ce polymère la formule

$$(CH_3)_3—C—(CHCl–CH_2)_{n-1}—CH=CH_2 \quad (I)$$

Dans cette communication, nous nous proposons de déterminer, par analyse cinétique, le mécanisme de cette catalyse. Pour justifier la formule I, il faut et il suffit que le processus comporte les trois réactions suivantes, où R est $(CH_3)_3C—$ et M est $CHCl=CH_2$

Initiation:

$$R^-, \overset{+}{M}gCl + M \xrightarrow{k_i} R—CHCl—CH_2^-, \overset{+}{M}gCl \quad (1)$$

Propagation:

$$RCHClCH_2^-, \overset{+}{M}gCl + M \xrightarrow{k_p} R—(CHClCH_2)—CHClCH_2^-, \overset{+}{M}gCl$$

$$R(CHClCH_2)_nCHClCH_2^- + M \xrightarrow{k_p} R(CHClCH_2)_{n+1}CHClCH_2^- \quad (2)$$

Arrêt:

$$R(CHClCH_2)_nCHClCH_2^-, \overset{+}{M}gCl \xrightarrow{k_t} R(CHClCH_2)_n—CH=CH_2 + MgCl_2 \quad (3)$$

PARTIE EXPÉRIMENTALE

Materiaux

Le chlorure de vinyle commercial est purifié, par barbotage dans une solution aqueuse concentrée de soude et séchage sur potasse en pastilles, puis il est piégé à froid dans un container en acier inoxydable.

Le solvant (THF), est séché au sulfate de sodium et distillé peu de temps avant l'emploi, sur sodium en ruban et hydrure double de lithium et d'aluminium, sous courant d'azote purifié.

Le catalyseur est obtenu par action directe d'un large excès de magnésium en tournures sur le chlorure de tertiobutyle en milieu THF. La solution limpide est décantée, filtrée et transférée sous atmosphère d'azote purifiée dans une burette. Une partie aliquote est dosée selon la méthode de Gilman.[3]

En vue de l'étude cinétique, on utilise aussi du butane normal (produit commercial purifié).

Polymérisation

L'opération est effectuée dans une enceinte en verre de 1000 cm³ maintenue à 25 ± 0,5° C, par un fluide thermostatique circulant dans un serpentin interne, et agité par voie électromagnétique. La charge comprend successivement le solvant, puis le butane, le monomère et enfin, après que l'équilibre thermique soit atteint, la solution catalytique. En fin de polymérisation la réaction est arrêtée par introduction d'acide chlorhydrique concentré.

Etude Cinétique

Selon un principe déjà publié par l'un de nous[2] des prélèvements sont effectués dans le milieu réactionnel au moyen d'une seringue hypodermique. Le liquide prélevé (environ 0,5 cm³) est introduit dans une enceinte de 500 cm³, préalablement vidée. La vaporisation totale est réalisée par chauffage de l'enceinte; un systéme d'agitation électromagnétique assure l'homogénéisation du mélange gazeux. Une partie aliquote du mélange est analysée par chromatographie en phase vapeur, ce qui permet d'obtenir le rapport molaire monomère/butane, R_t à l'instant t. Le taux de conversion est donné par la relation

$$\rho = 1 - R_t/R_0$$

Lorsque le rapport molaire butane/THF, dans le réacteur, est inférieur à 3×10^{-2}, la solubilité du monomère dans le THF n'est pas modifiée et la courbe d'étalonnage obtenue en portant la concentration introduite de monomère en fonction de la concentration observée par chromatographie est une droite passant par l'origine et dont la pente est 1. Si au contraire, la concentration en butane est plus élevée, la solubilité du monomère diminue; l'excès de monomère passe dans la phase gazeuse et se solubilise au cours de la polymérisation ce qui risque d'introduire une erreur non négligeable dans les mesures cinétiques.

Le chromatogramme comporte, outre le pic de butane et le pic de monomère un pic de THF beaucoup plus éloigné, ainsi qu'un petit pic de triméthylméthane qui provient d'une destruction partielle du catalyseur par les traces d'eau restant dans le monomère et le solvant. Cette destruction est instantanée car le pic de tertiobutane n'augmente pas avec le temps. Elle correspond à environ 3×10^{-3} moles de catalyseur désactivé.

Etude des Polymères

Le polymère formé, partiellement insoluble dans le THF, est séparé par précipitation; celle-ci est totale lorsqu'on utilise un mélange méthanol–eau; elle n'est que partielle si l'on utilise uniquement le méthanol; dans ce dernier cas, l'addition d'eau dans le filtrat permet de séparer les molécules peu polymérisées. Dans tous les cas, le chlorure de magnésium reste dans les solutions acidifiées par l'acide chlorhydrique.

La composition des différents produits est déterminée par analyse chimique centésimale. En admettant la formule I, on peut obteinr le degré de polymérisation moyen n. En effet, on aura

$$\text{teneur en carbone (\%)} = \frac{24_n + 48}{62{,}5n + 21{,}5} \times 100$$

$$\text{teneur en hydrogène (\%)} = \frac{3n + 9}{62{,}5n + 21{,}5} \times 100$$

$$\text{teneur en chlore (\%)} = \frac{35{,}5n - 35{,}5}{62{,}5n + 21{,}5} \times 100$$

Lorsque n est inférieur à 50, la précision des dosages est satisfaisante.

RESULTATS ET DISCUSSION

Trois expériences ont été effectuées selon les conditions précisées dans le Tableau I.

TABLEAU I
Conditions Expérimentales de Polymérisation

No essai	Temp., °C.	THF, g	Monomère, g	Butane, g	*t*-BuMgCl, moles $\times 10^2$	Durée, heures	Polymère isolé, g
III	25	278	144	12	1,47	22	15,8
V	25	371	131	11	9,0	25	66,3
VII	25	328	127	8	4,55	22	24,9 (a) +5,4 (b)

Les valeurs des taux de conversions en fonction du temps sont représentées par les courbes de la Figure 1.

Il n'existe pas de période d'induction décelable et le rendement de la polymerisation tend vers une limite dont la valeur dépend de la concentration en catalyseur.

L'absence de période d'induction tend à prouver que la réaction d'initiation est pratiquement instantanée, ou du moins rapide par rapport à la réaction de propagation; s'il n'en était pas ainsi, les courbes cinétiques présenteraient un point d'inflexion d'autant plus éloigné de l'origine des temps que la constante de vitesse d'initiation k_i serait plus petite. En

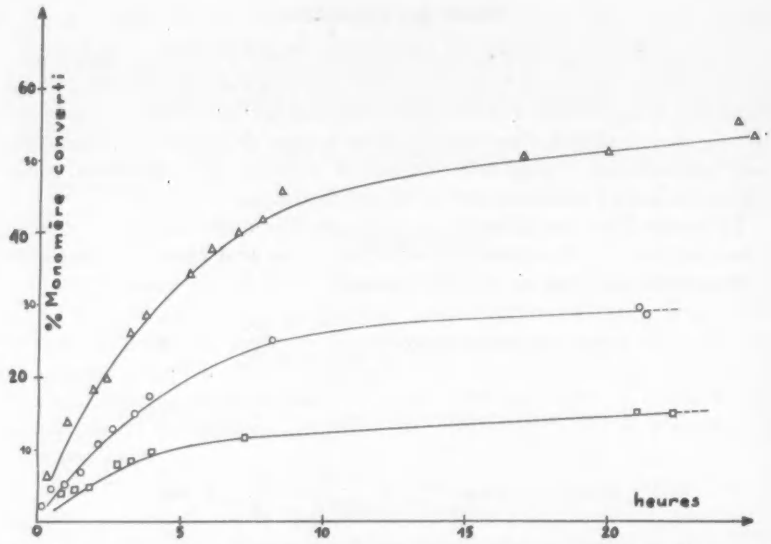

Fig. 1. Pourcentage de monomère converti en fonction du temps: (□) essai III; (○) essai V; (△) essai VII.

fait, la réaction d'initiation est la réaction normale d'addition de l'organomagnésien sur la double liaison polarisée du monomère, qui, ici, est présent en très grand excès. Du point de vue cinétique, tout se passe donc comme si le processus ne comportait que les réactions de propagation et d'arrêt.

La réaction de propagation est aussi une réaction d'addition d'un composé organomagnésien sur la double liaison du monomère.

La réaction d'arrêt est particulière aux monomères halogénés. Son existence est rendue probable par la structure des polymères obtenus d'une part, et d'autre part du fait de l'observation d'une limite à la polymérisation. La réaction d'arrêt correspond en effet à la disparition d'un anion polymère qui lui-même provient de la dissociation du chlorure de tertiobutyle magnésium. Si cette dissociation est totale, la limite de la polymérisation correspond à la consommation totale du catalyseur. La chromatographie permet de vérifier que l'organomagnésien est entièrement consommé au cours de la polymérisation; en effet, après arrêt du processus par introduction d'acide chlorhydrique, le pic de tertiobutane n'est pas plus grand que celui que l'on observe dans les prélèvements effectués au cours de la polymérisation. L'analyse chromatographique montre aussi que, si l'on fait réagir la solution catalytique fraîche avec l'acide chlorhydrique, la formation de tertiobutane est quantitative.

La consommation de monomère par la réaction d'initiation étant négligeable, seule la réaction de propagation rend compte du taux de monomère converti. Il en résulte que l'ordre apparent de la réaction par rapport au monomère doit être égal à un. Les droites parallèles représentées sur

la Figure 2, obtenues en portant la vitesse instantanée de polymérisation en fonction de la concentration actuelle en monomère, confirment cette prévision.

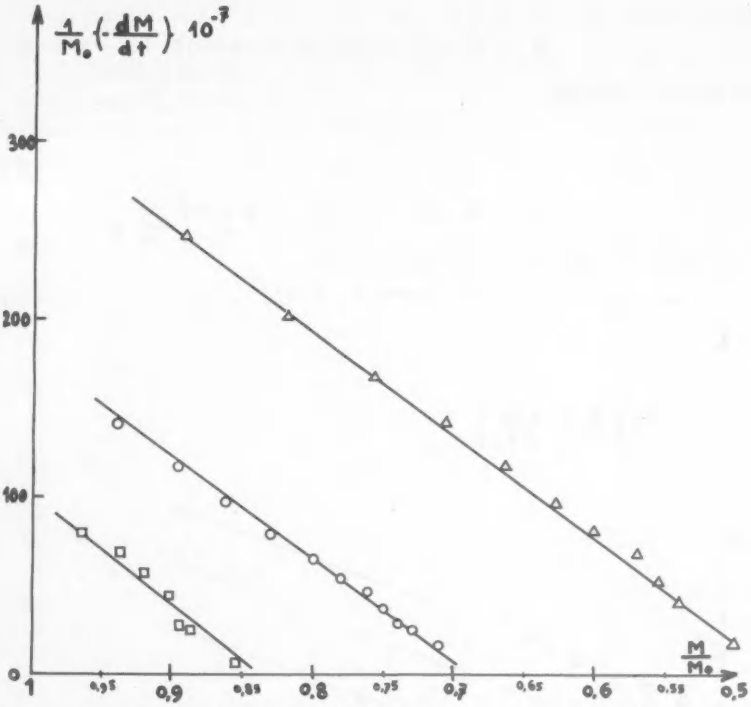

Fig. 2. Vitesses instantanées de polymérisation en fonction de la concentration courante en monomère: (□) essai III; (△) essai V; (○) essai VII.

Du point de vue cinétique, les réactions de propagation (2) et d'arrêt (3) s'écrivent

$$C\bar{n} + M \xrightarrow{k_p} C^-_{n+1} \qquad (2')$$

$$C\bar{n} \xrightarrow{k_t} P_n \qquad (3')$$

où C^-_n représente un anion polymère de degré de polymérisation n, M, le monomère, et P_n une molécule de polymère de degré de polymérisation n.

Nous avons donc

$$-dC/dt = k_t C \qquad (4)$$

et

$$-dM/dt = k_p \cdot CM \qquad (5)$$

où C est la concentration en anion polymère et M la concentration en monomère. En intégrant, on obtient:

$$C^- = C^-_0 \, e^{-k_t t} \tag{6}$$

et

$$M = M_0 \exp\{-(k_p/k_t)C_0 \, (1-e^{-k_t t})\} \tag{7}$$

ou encore, en prenant

$$\theta = e^{-k_t t}$$

$$C^- = C_0\theta \tag{6'}$$

$$M = M_0 \exp\{-(k_p/k_t) \, C_0 \, (1 - \theta)\} \tag{7'}$$

La relation (7') peut se mettre sous la forme

$$\log \, [(1/M) \, (-dM/dt)] = \log(k_p \cdot C_0) - (\log e) \, k_t \, t \tag{8}$$

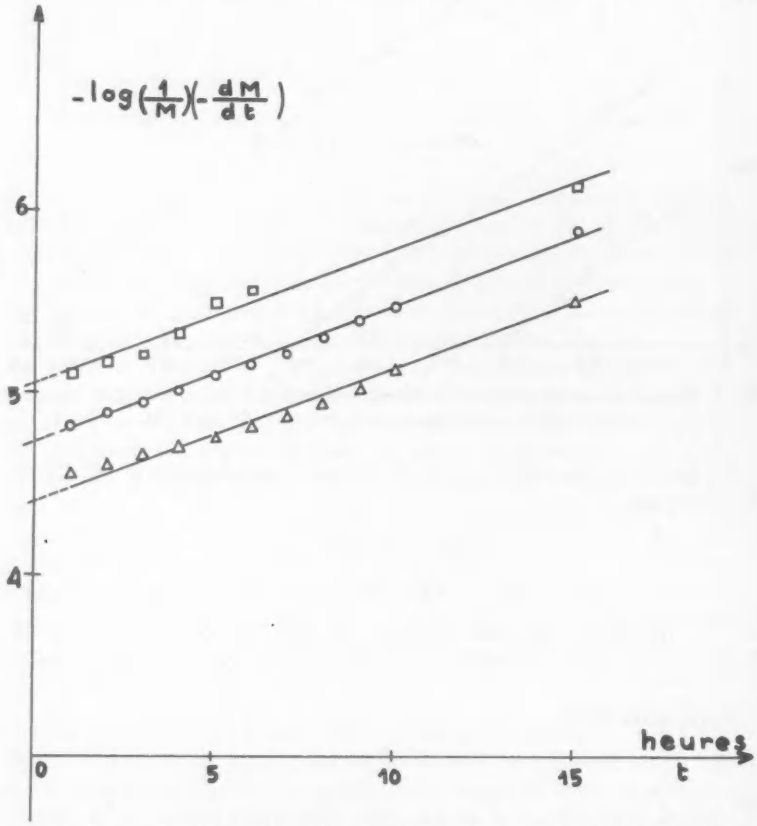

Fig. 3. Vérification de la relation (8): (□) essai III; (△) essai V; (○) essai VII.

En portant les valeurs expérimentales de log $[(1/M)\ (-dM/dt)]$ en fonction du temps, on doit obtenir des droites parallèles dont la pente donne k_t et les ordonnées à l'origine k_pC_0. Les droites sont représentées sur la Figure 3.

On trouve $k_t = 4{,}7 \pm 0{,}4 \times 10^{-5}$ sec^{-1} et pour $k_p\ C_0$ les valeurs respectives de $8{,}7 \times 10^{-5}$, $1{,}99 \times 10^{-5}$, et $3{,}98 \times 10^{-5}$.

La détermination de k_t permet de vérifier directement la relation (7')en portant log (M_0/M) en fonction de θ. La Figure 4 montre bien que l'on obtient trois droites concourantes au point $\theta = 1$. Leurs pentes, ainsi

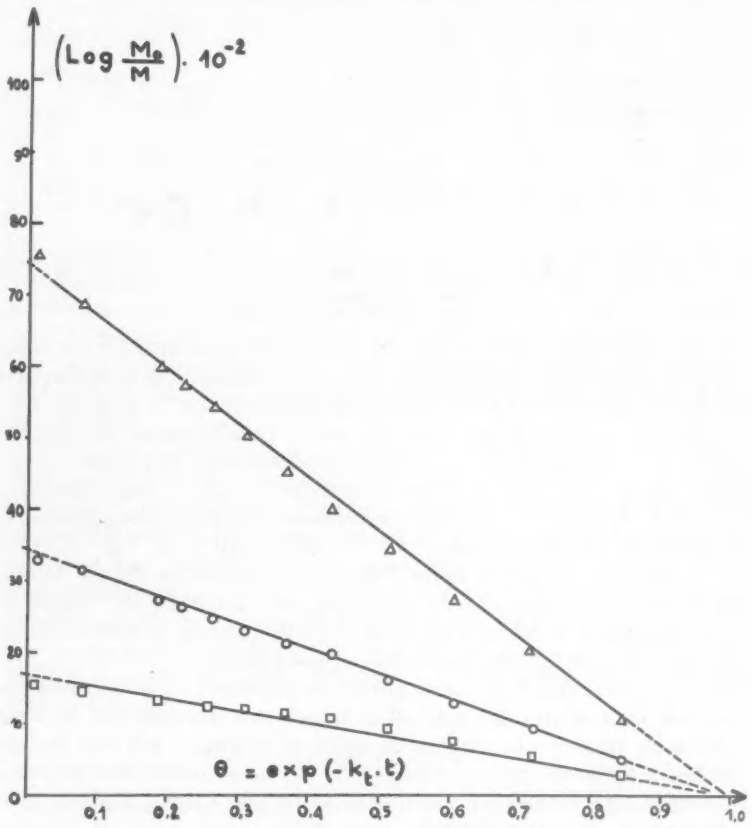

Fig. 4. Vérification de la relation (7'): (□) essai III; (△) essai V; (○) essai VII.

que leurs ordonnées pour $\theta = 0$ permettent une nouvelle détermination de k_pC_0. On trouve respectivement $8{,}0 \times 10^{-6}$, $1{,}62 \times 10^{-5}$, et $3{,}48 \times 10^{-5}$. Les ordonnées des points d'abscisse $\theta = 0$, correspondent à la limite de la polymérisation.

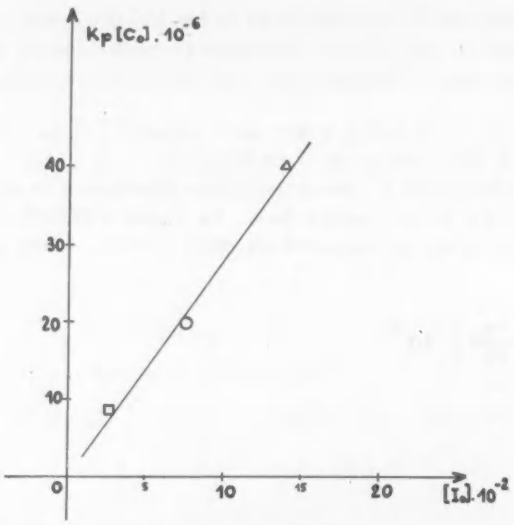

Fig. 5. Détermination de la constante de vitesse de propagation: (□) essai III; (△) essai V; (○) essai VII.

Nous avons admis la dissociation totale du catalyseur ainsi qu'une réaction d'initiation rapide et complète. Dans ces conditions, la concentration initiale en centres actifs C_0 est égale à la concentration en catalyseur I_0. Sur la Figure 5, nous avons porté les valeurs précédemment déterminées pour k_pC_0 en fonction de I_0. Les points expérimentaux se placent sur une droite passant par l'origine. Ceci montre qu'il y a bien proportionnalité entre C_0 et I_0. Si l'on admet que le coefficient de proportionnalité est 1, la pente de la droite donne $k_p = 2{,}6 \times 10^{-4} \pm 0{,}2 \times 10^{-4}$ sec^{-1}. En fait, puisque les traces d'eau contenues dans les réactifs décomposent une petite quantité de catalyseur, de l'ordre de 10^{-3} moles/l, C_0 est légèrement inférieur à I_0. L'erreur introduite sur la détermination de k_p est pratiquement négligeable si I_0 est assez grand.

Le mécanisme simple que nous proposons implique, en ce qui concerne les poids moléculaires des polymères formés, des conséquences qu'il est possible de vérifier. Le nombre de moles de polymère doit être égal au nombre de moles de catalyseur introduit. La masse moléculaire moyenne en nombre est donc théoriquement égale au rapport entre le poids de polymère formé et ce nombre de moles.

Dans le Tableau II nous avons reporté cette masse théorique ainsi que les masses moléculaires trouvées expérimentalement; ces dernières sont déterminées par analyse centésimale dont les résultats figurant dans le Tableau III.

Les écarts entre les masses moléculaires théoriques et expérimentales sont assez importants; mais les écarts entre les rendements théoriques et

TABLEAU II
Rendements et Masses Moléculaires Théoriques et Experimentaux

N° essai	Rendement theorique, g	Rendement, g	I_0 moles × 10^2	M_n theor.	n exp.	M_n exp.
III	22,16	15,8	1,47	1500	100	6270
V	71,9	66,3	9,0	800	17	1080
VII	37,0	30,3	4,55	815	33	2060

TABLEAU III
Analyse Centésimale et Degré de Polymérisation des Polymeres

N° essai	C, %	n_C	H, %	n_H	Cl, %	n_{Cl}	Poids polymere, g
III	39,03	75–175	4,98	100	56,36	80–00	15,8
V	41,69	19	5,50	18	51,5	14–15	66,3
VII (a)	39,9	42	4,92	100	55,15	45–46	24,9
VII (b)	42,0	17–18	5,62	14–15	51,2	13–14	5,4

expérimentaux sont aussi grands; on peut penser qu'ils proviennent des molécules très peu polymérisées qu'il n'est pas possible de précipiter. En admettant que le polymère qui se forme dans le milieu réactionnel possède bien la masse théorique, on peut calculer la masse moléculaire moyenne des polymères non précipités. On trouve respectivement les valeurs de 520, 150, et 250 ce qui correspond à des degrés de polymérisation de 8, 3, et 4 environ.

Pour tester la valeur de cette explication, il faudrait calculer la distribution théorique des masses moléculaires. Dans les conditions expérimentales présentes il est impossible d'effectuer ce calcul, car on aboutit à des équations différentielles que les moyens mathématiques normaux ne permettent pas d'intégrer; le calcul n'est possible que lorsque la concentration en monomère reste constante. Mais si l'on admet l'égale probabilité de la réaction d'arrêt en fonction de la taille de l'anion polymère, il est certain que le nombre de molécules de degré de polymérisation inférieure à 5, molécules probablement solubles dans le milieu de précipitation, est loin d'être négligeable.

CONCLUSION

Le mécanisme que nous proposons est particulièrement simple, mais parait assez bien rendre compte des résultats expérimentaux. Il faut remarquer que ce n'est que parce que la réaction d'initiation est ici particulièrement rapide que nous avons pu déterminer les valeurs des constantes de vitesses de propagation et d'arrêt. Mais ces valeurs doivent être conservées dans des polymérisations du chlorure de vinyle utilisant d'autres catalyseurs organomagnésiens chlorés, à la condition de conserver le milieu solvant. Cependant, pour bien connaitre la polymérisation anionique du chlorure de

vinyle, il reste à déterminer l'influence de nombre de paramètres expérimentaux et c'est pourquoi nous poursuivons nos recherches dans ce domaine.

Les auteurs tiennent à remercier M. J. Guillot qui a aidé à la mise au point des analyses chromatographiques.

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Résumé

La polymérisation anionique du chlorure de vinyle, catalysée par le chlorure de tertiobutyle mangésium, en milieu tétrahydrofurane, est étudiée du point de vue cinétique, au moyen de la chromatographie en phase vapeur. La réaction d'initiation peut être considérée comme très rapide, et les réactions de propagation et d'arrêt (par transfert de chlore) suffisant à expliquer la cinétique observée. A 25°C, les constantes de vitesse de ces deux réactions sont respectivement $k_p = 2{,}6 \times 10^{-4}$ et $k_t = 4.7 \times 10^{-5}$ sec^{-1}.

Synopsis

Kinetics of anionic polymerization of vinyl chloride with *tert*-butylmagnesium chloride as catalyst and tetrahydrofuran as solvant, were studied by vapor phase chromatography. The initiation réaction can be judged to be very rapid, and propagation and termination (by transfert of chlorine) reactions are sufficient to explain the observed kinetics. At 25°C, rates constants of two reactions are respectively, $k_p = 2.6 \times 10^{-4}$ and $k_t = 4.7 \times 10^{-5}$ sec.$^{-1}$.

Zusam menfassung

Die Kinetik der anionischen Vinylchloridpolymerisation bei Katalyse mit *tert*-Butylmagnesiumchlorid in Tetrahydrofuranlösung wird gaschromatographisch untersucht. Die Annahme einer sehr schnellen Startreaktion, einer Wachstumsreaktion und einer Abbruchsreaktion durch Chlorübergang genügt zur Erklärung der beobachteten Kinetik. Die Geschwindigkeitskonstanten dieser beiden Reaktionen sind bei 25°C: $k_p = 2{,}6$ 10^{-4} sec^{-1} und $k_t = 4{,}7$ 10^{-5} sec^{-1}.

Discussion

T. Tsuruta (*Kyoto University, Japan*): Do you have some concrete evidence for anionic mechanism in your polymerization of vinyl chloride?

A. Guyot: We have not direct proof of the anionic character of the mechanism; but the kinetics and the structure of the polymer (nature of the end groups, high cristallinity, low molecular weight) are in agreement with an anionic mechanism. Further, the experiments were carried out in the complete absence of oxygen and light.

B. Eroussalimsky (*Léningrad, U.R.S.S.*): Have you tried to polymerize the vinyl chloride in hydrocarbon media?

A. Guyot: No, but we plan to do that.

B. Eroussalimsky: Have you only kinetical proofs of the mechanism of termination or also some data of the loss of catalyst?

A. Guyot: If a fresh solution of catalyst is reacted with water or hydrochloric acid, one can observe the formation of tertio-butane, by chromatographic analysis. After the

polymerization experiments, we have reacted the solution with hydrochloric acid and did not observe any formation of tertio-butane.

D. C. Pepper (*Dublin, Ireland*): It is most interesting to learn that the kinetics of this homogeneous anionic polymerization are virtually identical with those we have found for the *cationic* polymerization of styrene by H_2SO_4 (Hayes and Pepper, *Proc. Chem. Soc.*, (1958); *Proc. Roy. Soc.*, **A263** (1961)). In this system (unlike the related reaction initiated by perchloric acid) there exists a fairly rapid termination process, and the characteristic non-stationary overall kinetics follow in consequence.

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Polymerization of Propylene Oxide Catalyzed by Trimethyl Aluminum

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In a previous investigation[1] it was shown that the polymerization of propylene oxide in the presence of catalytic amounts of trimethylaluminum and water could be divided into three successive stages:

(*a*) A fast reaction at 0°C. giving low polymer (M.W. < 1000), which quickly slowed to an apparently negligible rate at about 20% conversion in 15 hr.;

(*b*) On heating the product of (*a*) to 80°C., a further rapid conversion (30–40%) of propylene oxide to low polymer, which again died away after approximately 1 hr., to be followed by.

(*c*) A very slow reaction in which high molecular weight, partly stereoregular polymer was formed.

In the absence of water, stages (*a*) and (*b*) were observed, but not stage (*c*). Since attention was primarily focused on the stereospecific mechanism of stage (*c*), which required a temperature of 80°C. to give a reasonable rate, the kinetic measurements were confined to this temperature, as accurate measurements at both 0 and 80°C. for the same reaction were not practicable using sealed dilatometers. Thus, stage (*a*) was not investigated in detail, but was assumed to involve the replacement of methyl groups by short polymer chains, analogous to the corresponding reaction between ferric chloride and propylene oxide,[2] and hydrolysis at the end of stage (*a*) indicated that one methyl group remained attached to each aluminum atom in the absence of water.

However, as the general kinetic picture of stage (*b*) emerged, it became clear that stage (*a*) was both more critical and more complex than had been supposed, and we have therefore examined the kinetics of the reaction at 0°C. in detail. The purpose of this communication is to present the results briefly, together with some relevant work on the reaction between trimethylaluminum and ethanol, and to outline our present ideas on the mechanism of the stereospecific stage of the polymerization.

EXPERIMENTAL METHODS

The reaction was followed in sealed dilatometers at 0°C., with methylene chloride as solvent, and the concentrations of the reagents were similar to

those used in the previous work.[1] The reagents were distilled into the dilatometers under high vacuum, and kept frozen in liquid nitrogen until mixed in the thermostat, when readings were commenced. During the reaction methane was evolved, and measurements on the rate of evolution of methane were made separately on a larger scale in reaction vessels attached to a vacuum line designed for this purpose.

RESULTS

It is convenient, as before, to consider the reactions in the presence and absence of catalytic amounts of water separately, and these will be referred to as the "wet" and the "dry" reactions.

The Dry Reaction

The results confirmed the previous general conclusion that the reaction at 0°C. stopped before all of the monomer was consumed, but showed that the period of 15 hr. previously allowed for the completion of this reaction was insufficient. This also applied to wet reactions when the ratio $[H_2O]/[AlMe_3]$ was less than 0.3.

This immediately raises the possibility that stages (*a*) and (*b*) may in fact be parts of the same reaction at different temperatures. We believe this to be so for the following reasons.

(*1*) The measured rate of 0°C. after 15 hr. corresponds to that calculated from the initial rate of stage (*b*) at 80°C., assuming the activation energy of 14.8 kcal. mole^{-1} found for stage (*b*).

(*2*) The variation of the rate of 0°C. after 15 hr. with initial concentrations of reagents corresponds to that observed for the initial rate of stage (*b*).

(*3*) The final yield of low polymer at 0°C. corresponds to the sum of the yields of stages (*a*) and (*b*).

(*4*) In the presence of water, the reaction at 0°C. occurs in two stages, corresponding to stages (*a*) and (*c*) of the reaction at 80°C., without any intermediate stage.

This conclusion invalidates the kinetic results previously obtained from measurements of the initial rate of stage (*b*), which is now seen to be an arbitrary fraction of a more comprehensive reaction, whose main features can be summarized as follows.

Kinetics. The course of a dry reaction at 0°C. is accurately described by the following equation:

$$\frac{1}{[M_f]} \ln \frac{[M] - [M_f]}{[M]} = -k_i t + \text{const.} \qquad (1)$$

or, in its differentiated form, the instantaneous rate

$$-d[M]/dt = k_i[M]([M] - [M_f]) \qquad (2)$$

where [M] is the instantaneous and [M_f] the final concentration of propylene oxide.

If [M_0] is the initial concentration of propylene oxide, and [C_0] the initial concentration of catalyst expressed as [$AlMe_3$], then the final yield of polymer expressed in terms of monomer consumed is given by:

$$[M_0] - [M_f] = K_y[C_0][M_0] \tag{3}$$

where $K_y = 12.5 \pm 2.5$ l. mole^{-1}. This relation holds for values of [C_0] up to 0.06 mole l.$^{-1}$, but at higher values the order in [C_0] decreases.

If we assume that the [M] term in eq. (2) is due to the disappearance of monomer in the propagation reaction (i.e., that propagation occurs by a bimolecular reaction between monomer and active centers), and that the [M] − [M_f] term is related to the concentration of active centers, then, if [C*] is the instantaneous concentration of active centers:

$$-d[M]/dt = k_p[C^*][M] \tag{4}$$

and eq. (2) can be simply interpreted as a nonstationary reaction in which active centers initially present disappear by a process which is first-order both relative to their own concentration and to [M]. Thus:

$$-d[C^*]/dt = k_t[C^*][M] \tag{5}$$

Since by definition [M] = [M_f] when the rate is zero (i.e., when [C*] = 0), eq. (2) can easily be derived from eqs. (4) and (5).

The value of k_t, though constant for any one reaction, shows a linear variation with the initial catalyst concentration, $k_t = k_t'$ [C_0], and eqs. (5) and (2) are better written as:

$$-d[C^*]/dt = k_t'[C_0][C^*][M] \tag{5a}$$

$$-d[M]/dt = k_t'[C_0][M]([M] - [M_f]) \tag{2a}$$

Values of k_t' were determined over a fivefold range of monomer (0.50–2.87 mole l.$^{-1}$) and catalyst (0.02–0.09 mole l.$^{-1}$) concentrations, and was found to be constant within experimental error, with an average value of 0.6 ± 0.3 l.^{2} mole^{-2} hr.$^{-1}$ at 0°C. Values of k_t' were also obtained at 10 and 25°C., giving an activation energy of $E = 16.4$ kcal. mole^{-1} for the termination step.

Unfortunately, the determination of k_t' does not enable us to find k_p from initial rate measurements, since [C*] is not known, and measurements of the methane evolution during the reaction indicate that [C_0*] is not equal to [C_0]. Nor can k_p be derived from the molecular weight of the product, since this is governed by a rapid transfer reaction. However, if [C_0*] is taken as equal to [C_0]/4 based on the evolution of methane, then $k_p = 1.9 \pm 0.2$ l. mole^{-1} hr.$^{-1}$

Products. The polymeric product isolated after hydrolysis, previously described as a liquid polymer with a molecular weight less than 1000, was found to be composed of a fraction A which was appreciably volatile

in vacuo at room temperature, and a fraction B which was involatile. The molecular weight of B, which comprised about 70% of the total yield, was examined cryoscopically, and found to have a value of 235 ± 25 which was independent of both $[C_0]$ and $[M_0]$. Its infrared spectrum was almost identical with that of high molecular weight amorphous polymer, and showed no unsaturation. The concentration of —OH groups was small, corresponding to approximately one —OH group per 20 ether links. Since liquid polyethers of this type are quite hygroscopic, some of these —OH groups may be due to water picked up during measurement, as some contact with the atmosphere was unavoidable. We conclude, therefore, that B is largely cyclic tetramer.

Fraction A consists of cyclic dimer and trimer which can be distilled from the total product before hydrolysis, but also contains an appreciable fraction which can only be removed after hydrolysis, and which shows a relatively larger —OH peak. We have not yet completed our examination of the volatile products, whose most puzzling feature is the absence of the unsaturation expected in view of the evolution of methane. A possible explanation is the formation of an unsaturated alcohol sufficiently volatile to be removed with the unchanged monomer and solvent, and this is being investigated.

Evolution of Methane. Previous work[1] on the evolution of methane in the dry reaction is open to objection on the ground that the small amount of gas evolved (0.5 moles methane/Al atom) might be due to reaction of the catalyst with adventitious water or alcohol rather than with the monomer. This criticism is both valid and hard to meet satisfactorily. Small traces of water have a much greater effect on the rate of methane evolution than on the rate of polymerization, which is affected only insofar as a trace of water converts a fraction of the catalyst into a slightly more active form. We have found, however, that it is possible to distinguish kinetically between gas evolution due to water and that due to the dry reaction.

In a series of experiments[3] on the reaction between trimethylaluminum and ethanol in hexane solution, it was found that equimolar quantities ($\approx 10^{-2}$ mole $l.^{-1}$) react almost instantaneously, evolving 0.5 moles of methane/Al atom. This is followed by a very much slower first-order reaction with a half-life of about 3 min., in which the remaining 0.5 moles methane/Al are evolved. With water in place of ethanol, at half the molar concentration (i.e., equimolar concentration of active hydrogen), a similar course is followed, both in the presence and absence of propylene oxide. In the absence of propylene oxide, precipitation occurs; but in the presence of propylene oxide there is no precipitate, and 0.5 moles methane/Al are evolved almost instantaneously, followed by slower evolution of a further 0.5 moles/Al which is complete in several hours.

When propylene oxide and catalytic amounts of trimethylaluminum were mixed in hexane solution in the absence of water, the course of methane evolution was quite different. Gas was evolved slowly, in parallel with

the rate of polymerization, and the two reactions of gas evolution and polymerization had the same half-life ($\approx$ 20 hr.). The total amount evolved corresponds to 0.25 $\pm$ 0.02 moles methane/Al, and this cannot be due to adventitious water or alcohol, since the quantity required to produce this amount of gas would have reacted much more rapidly and in two distinct stages. The previous figure[1] of 0.5 moles methane/Al was obtained from total gas measurements only, and must be regarded as less reliable, since the absence of traces of water was not proved. The number of methyl groups/Al remaining after the polymerization and gas evolution had ceased was also redetermined by hydrolysis of the reaction mixture. This measurement is complicated by the heterogeneity of the hydrolyzed mixture, which slows down the later stages of gas evolution, and also by the uncertainty in solubility coefficients introduced when a large excess of methanol–water mixture is used for hydrolysis. Previous estimates are now known to be too low because of these effects. Complete hydrolysis of the final reaction mixture, using a slight excess of water, gave a quantity of methane equivalent to 2.75 $\pm$ 0.02 methyl groups/Al, and therefore, within narrow limits, all of the methyl groups originally attached to aluminum are accounted for as methane evolved. The figures for gas evolved during the reaction and on final hydrolysis, though surprising in view of current theories, are thus mutually confirmatory.

The Wet Reaction

Evolution of Methane. In the presence of catalytic amounts of water up to half the molar concentration of trimethylaluminum ($\rho = [H_2O]/[AlMe_3] \leq 0.5$), the primary event is the evolution of 1.0 moles methane/mole H_2O almost instantaneously. At this point, gas evolution slows markedly, and we conclude that the rapid evolution corresponds to the formation of a dimeric catalyst species, Al_2Me_5OH, designated C^f, whose initial concentration $[C_0^f] = [H_2O]$ when $\rho \leq 0.5$. The formation of Al_2Me_5OH rather than $AlMe_2OH$ as the first step is supported by a similar result in the reaction between the metal alkyl and ethanol, where there is a clear discontinuity in the rate of gas evolution at a point corresponding to the formation of $Al_2Me_5OC_2H_5$. It is possible that the formation of C^f involves propylene oxide, but the reaction is so fast that we have not yet been able to determine whether the rate depends on $[M_0]$ or not. It is certainly complete before any appreciable polymerization has taken place.

The kinetics of the polymerization reaction also confirm the formation of a catalyst species involving two Al atoms per H_2O added, but show that C^f is not itself the active catalyst. This is formed from C^f in an initiation reaction which involves propylene oxide, and during which further methane is evolved. Experimentally at $\rho = 0.5$, the initial rapid evolution of gas, coincident with the start of polymerization, is followed by a slower evolution of a further 1.0 moles methane/H_2O, extending over several hours, dur-

ing which the polymerization, in contrast to the dry reaction, shows an initial steady state. During the remainder of the primary reaction, and throughout the secondary reaction, no further gas evolution was detected. We have not yet completed accurate measurements on the gas evolved on final hydrolysis at $t = 312$ hr., but preliminary results at $\rho = 0.5$ indicate an amount corresponding to 2.0 methyl groups/Al, with a possible error of 10%. If 2.0 is, in fact, the true value, then as in the dry reaction, all of the methyl groups originally attached to the metal atom appear as methane evolved. This implies that none are transferred to polymer chains during the reaction, and that the active centers involves Al atoms to which two methyl groups are still attached.

Kinetics. At constant $[M_0]$, and $\rho \leq 0.5$, the initial rate R_i depends only on $[H_2O]$, but the maximum value obtained by increasing the water concentration is reached at $\rho = 0.5$, and therefore depends on $[C_0]$. This maximum R_i is approximately five times greater than the average rate over the first hour of the corresponding dry reaction. As ρ is increased from 0.5 to 1.0, the value of R_i decreases again to approximately one fourth of its maximum value, and at $\rho = 0.8$–1.0, precipitation may occur. We have found, however, that this depends upon the method of mixing the reagents, and provided that both the catalyst and water are diluted with solvent and propylene oxide before thawing and mixing, precipitation does not occur at $\rho < 1.0$.

This kinetic behavior is consistent with the view that the addition of water leads to the quantitative formation of a catalyst involving two moles $AlMe_3$ per mole of water, and that this is more active than either $AlMe_3$ alone (dry reaction) or species with a higher degree of oxygen substitution ($\rho > 0.5$). When ρ is greater or less than 0.5, this catalyst is present together with one of the less active catalysts, and R_i is composite, but at $\rho = 0.5$ all of the catalyst is initially in the form C^t, and the kinetics are then characteristic of the wet active center exclusively. The following results, therefore, relate to wet reactions in which $\rho = 0.5$, i.e., water is always present in molar concentration equal to $[AlMe_3]/2$.

The overall reaction shows two successive stages, viz., a relatively fast reaction which is essentially similar over most of its course, both in kinetics and products, to the dry reaction; followed by a very slow reaction corresponding to state (*c*) of the wet reaction at 80°C., which gives high molecular weight, partly stereoregular polymer. For convenience, these are referred to as the primary and secondary wet reactions, respectively.

The Primary Wet Reaction

As in the dry case, this reaction is described by eq. (1) over most of its course, but with the following differences.

(*1*) The value of $[M_f]$ is taken as the monomer concentration corresponding to the point of transition from the primary to the secondary reaction, at which the rate is approximately 1/500 of its initial value, rather than zero as in the dry reaction;

(2) The value of k_t obtained by applying eq. (1) is greater than that for the dry reaction by a factor of approximately twenty. Thus, for $[M_0] = 1.43$ and $[C_0] = 8.62 \times 10^{-2}$ mole l.$^{-1}$

$$k_t \text{ (dry)} = 0.032 \text{ l. mole}^{-1} \text{ hr.}^{-1}$$

$$k_t \text{ (wet)} = 0.70 \text{ l. mole}^{-1} \text{ hr.}^{-1}$$

This is a reflection of the fact that the primary wet reaction is complete in 10–12 hr., compared with 150–200 hr. for dry reaction. Since the final conversions are comparable, either k_p or the number of active centers, or both, must be correspondingly greater in the wet reaction. The value of k_t for the latter appears to be independent of $[C_0]$, in contrast to the dry case, and has an average value of 0.6 ± 0.1 l. mole^{-1} hr.$^{-1}$. The random scatter in this value is smaller than in the dry k_t', where the rates are much lower, and the error in measurement proportionally greater.

(3) The plot of eq. (1) shows a decreasing negative deviation from a straight line over the first few hours of the reaction. This appears in the conversion-time curve as the period of constant initial rate already referred to, which is not present in the dry reaction. If we assume that the termination reaction (5) operates throughout the initial period, the existence of a steady state argues the presence of an initiation reaction in which active centers are produced from C^i. Various orders in C^i and monomer have been tested empirically for this reaction, and the closest fit to the experimental results is given by the simple equation:

$$d[C^*]/dt = k_i[C^i][M_0] \tag{6}$$

where $d[C^*]/dt$ is the rate of production of active centers and $[C^i]$ the instantaneous concentration of the dimeric catalyst species previously described, present initially in concentration $[C_0^i] = [H_2O] = [C_0]/2$. (The concentration of monomer involved in eq. (6) should, strictly speaking, be the instantaneous concentration [M], but this can be taken as equal to $[M_0]$ over the initiation period without serious error, to facilitate integration of the composite differential equation.) In conjunction with eqs. (4) and (5), this gives the following relation:

$$k_t([M] - [M_f]) - R/[M] = k_p[C_0^i] \exp\{-k_i[M_0]t\} \tag{7}$$

where $R = -d[M]/dt$ is the instantaneous rate of polymerization at time t. This holds over the whole course of the primary wet reaction, reducing to eq. (2) when t is large. Writing eq. (7) in the form:

$$\ln\{k_t([M] - [M_f]) - R/[M]\} = \ln(k_p[C_0^i]) - k_i[M_0]t \tag{8}$$

it can be seen that by plotting the left-hand side of eq. (8) against t, the value of k_t can be obtained from the slope of the resulting straight line, and $k_p[C_0^i]$ from the intercept. If, as seems probable, $[C_0^i] = [C_0]/2$, then k_p can also be obtained explicitly.

TABLE I

	Velocity constant at 0°C., l. mole^{-1} hr.$^{-1}$	Activation energy, kcal. mole^{-1}
Initiation	0.4 ± 0.1	7.3
Propagation	20.0 ± 4.0	18.2
Termination	0.6 ± 0.1	14.5

In this way we have obtained values of k_t and k_p over a range of reagent concentrations, and these are constant within the limits indicated in Table I. The corresponding activation energies were obtained over the range −20 to +25°C., with an estimated possible error of 10% for the termination, and 20% for the initiation and propagation values.

Products. The product of the primary wet reaction, obtained by hydrolyzing the reaction at [M] = [M$_f$], was practically identical with the product of the dry reaction, consisting mainly of tetrameric cyclic polymer, together with some volatile cyclic dimer and trimer. Analysis by vapor-phase chromatography showed, however, that there was also an additional component, which has not yet been identified, but is believed to be an alcohol boiling in the range 100–150°C. There was also present a very small amount (<1%) of partly crystalline polymer with a molecular weight in the range 1–2 × 10^4. This could be due to slight overlap into the region of the secondary reaction as an experimental error; alternatively, the two reactions may be concurrent to some extent.

Effect of Ether and Dioxane. Dioxane has been used as solvent for the related polymerization of propylene oxide using diethyl zinc as catalyst,[4] and to allow comparison we have studied the effect of added dioxane, and also of diethyl ether, on the $AlMe_3$-catalyzed reaction. Both of these additives lowered the initial rate R_i, and over the range [A] = 0.5–6.0 mole l.$^{-1}$ the following relation was found to hold:

$$1/R_i = k_a[A] + \text{const.}$$

where [A] is the molar concentration of additive. The values of k_a found for ether and dioxane were 4.2 and 7.2 l.^{2} mole^{-2} hr.$^{-1}$ (±10%) respectively. Thus dioxane is nearly twice as effective as ether in reducing the initial rate.

This reciprocal relationship also applied to the variation of the apparent k_p and k_t with [A], and we attribute the effect to a decrease in the number of effective centers due to formation of a labile inactive complex with the additive:

$$[C^*] + [A] \overset{K_A}{\rightleftharpoons} [C^*\cdot A]$$

This gives the relation:

$$1/k_t'' = 1/k_t + (K_A/k_t)[A]$$

where k_t'' and k_t are the termination constants in the presence and absence of additive, which was found experimentally. A similar relationship holds for k_p, and the values of K_A, the equilibrium constant for the complex formation, derived are given in Table II.

TABLE II

	K_A, l. mole^{-1}	
	Ether	Dioxane
From k_p'' variation	0.35	2.6
From k_t''variation	0.35	1.4

In the case of ether, the constancy of K_A supports the view that it affects the propagation and termination steps simply by reducing the concentration of effective centers. The values obtained for dioxane indicate that it coordinates to the active center more strongly than ether, but it appears to affect the propagation more than the termination step. If the basic effect is, as we suggest, due to a reduction in [C*], this would indicate the presence of a subsidiary effect in dioxane, possibly associated with the presence of two etheric groups, which either decreases the rate of propagation or increases the rate of termination independently of the basic effect.

The initiation constant k_i, unlike k_p and k_t, is more affected by ether than dioxane, which had little or no effect even at a concentration of 7.0 mole l.$^{-1}$. Ether reduced k_i to 0.07 ± 0.02 l. mole^{-1} hr.$^{-1}$, but this showed no clear variation with concentration at 2.0–5.0 mole l.$^{-1}$. There may be a reciprocal relation of the type found for k_p and k_t, but our results do not warrant any definite conclusions on this point, and it is possible that the relation is more complicated, since a different catalyst species (C) is involved.

The Secondary Wet Reaction

This reaction, which corresponds to stage (*c*) of the reaction at 80°C., is extremely slow at 0°C., and the rate could not be measured very accurately in apparatus designed to deal with the much faster primary reaction. We have not, therefore, attempted any exact kinetic picture of the secondary reaction at 0°C., and the rate measurements which are briefly summarized in the following are given only as a general indication. The high molecular weight product has, however, been examined in some detail.

Kinetics. The secondary reaction was normally followed for a period of 300 hr., during which a shrinkage corresponding to 10–15% conversion was observed, with little fall-off in rate. Since there was no well-defined initial rate, due to overlap with the end of the primary reaction, the rate at 300 hr. from initial mixing (R_{300}) was taken as characteristic, and is given approximately by the following empirical relation:

$$R_{300} = 4 + 10^{-3}[M_0][C_0] \text{ mole l.}^{-1} \text{ hr.}^{-1}$$

where $[M_0]$ and $[C_0]$ are the initial concentrations of epoxide and $AlMe_3$ at the time of mixing. This, however, does not establish the order of the reaction, at least with regard to monomer, since at $t = 300$ the instantaneous value of [M] is usually less than half of $[M_0]$. The variation of R_{300} with the instantaneous value of [M] at $t = 300$ indicates that either the order in [M] is fractional ($\approx 1/2$) or that it is first-order when $[M] < 0.5$ mole $l.^{-1}$, and tends to zero-order at higher values. This is consistent with the general observation that the decrease in rate over the period 200–300 hr. approaches zero at $[M] = 1.5$ mole $l.^{-1}$.

Products. The polymeric product was normally isolated after hydrolysis at $t = 312$ hr. (60–80% conversion), but we have also carried out several experiments on a larger scale with arrangements for removing samples of the reaction mixture at various conversions. The final product comprises that of the primary reaction already described, together with high molecular weight polymer in quantity corresponding approximately to the shrinkage observed in the secondary reaction.

In previous work,[1,2] the similar polymer obtained at 80°C. was divided into a crystalline and an amorphous fraction by precipitation of the former from methanol at 0°C., and no distinction was made between the amorphous products due to the primary and secondary reactions. It has since been shown[7] that methanol is an unsuitable solvent for this purpose, giving a complicated separation which may be three-phase, and which is influenced by the molecular weight as well as the tacticity of the polymer. Variations of crystalline/amorphous yield with the ratio $[H_2O]/[AlMe_3]$ previously reported[2] are now thought to be misleading. In the present work, we have carried out a more extensive fractionation, in which the products of the primary reaction were separated from the high molecular weight polymer, and the latter divided into several fractions of differing degrees of crystallinity. The methods used were similar to those described by Booth, Jones, and Powell[4] in their examination of the closely allied polypropylene oxide obtained with diethyl zinc as catalyst.

The results show that the products characteristic of the primary reaction remain either unchanged, or show a slight increase, throughout the course of the secondary reaction, and constitute about $\frac{4}{5}$ of the total yield. The remaining $\frac{1}{5}$ consists of high molecular weight polymer formed in the secondary reaction, during which the molecular weight increased with conversion from 10^4 to 10^6 approximately. Various fractions of this polymer separated according to degree of crystallinity had the same intrinsic viscosity, and it appears to have the same characteristics as that studied by Booth, Jones, and Powell, viz., a wide variation in degree of isotacticity superimposed upon a wide distribution of molecular weight. This means that there is no sharp difference between random and regular high polymer, and individual chains will consist of a block copolymer of regular and irregular sequences in varying proportions. For purposes of comparison, the degree of tacticity of the high polymer was arbitrarily estimated on the fraction insoluble in cyclohexane at 20°C. This was found to comprise

approximately 30% of the total high polymer, this figure being independent of reagent concentrations and of the conversion.

The molecular weight of the high polymer appeared to vary directly with the initial monomer concentration and to be independent of the catalyst concentration, but this could not be determined very precisely, since apart from the large-scale sampling experiments, the actual weight of high polymer obtained in any one experiment was small ($\approx$0.1 g.). The number of high molecular weight polymer chains formed is very much less than the number of Al atoms present. At the end of the primary reaction, there are approximately three molecules of cyclic polymer formed per Al, but in the secondary reaction, the number of high molecular weight chains per Al atom is of the order of 10^{-3}.

DISCUSSION

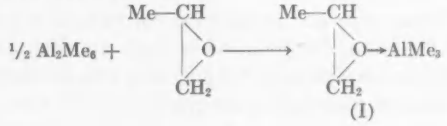
In comparing the reactions in the presence and absence of water, the most striking difference is the formation of high molecular weight polymer in the secondary part of the wet reaction. (It does not follow, however, that water is a necessary ingredient for stereoregulation, as has been suggested,[1] since it is now clear that if the dry reaction were also stereospecific the effect would not be detected in the product by the methods used for high polymer.)

The similarities are equally striking. The dry reaction and the primary wet reaction both show relatively simple kinetics, which, apart from the initiation reaction, differ only in the values of the rate constants involved, and the products of these two reactions are almost indistinguishable. We conclude that the dry and the primary wet reactions involve essentially the same type of active center, which differs from that of the secondary wet reaction. This difference, which we believe to be mechanistic rather than of kind, is discussed later.

Nature of the Active Center in the Dry Reaction

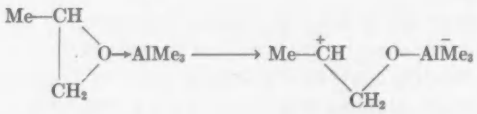
The kinetics of the dry reaction show that the active catalyst is formed immediately on mixing and subsequently disappears by a first-order process. There is no initial rapid evolution of methane, however, and therefore no loss of methyl groups from Al in forming the active centers, since all of the methyl groups are eventually accounted for as gas evolved. This rules out the type of active centre previously suggested[1] based on the coordinate anionic mechanism of Price and Osgan,[5] in which one or more of the methyl groups attached to Al is replaced by an alkoxy group.

We conclude, therefore, that the active center must be cationic, with the $AlMe_3$ acting simply as an electron acceptor. Initiation might involve the formation of a carbonium ion:

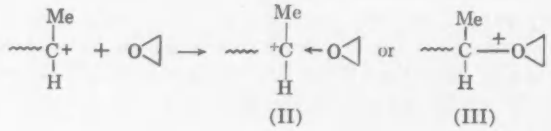


(I)

followed by:



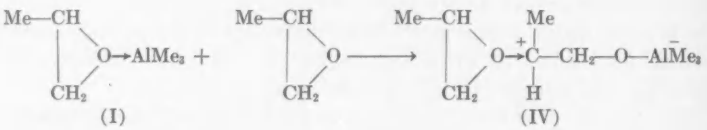
but this is unlikely in view of the relatively feeble strength as Lewis acids of the catalysts giving this type of polymerization ($AlMe_3$, $FeCl_3$, $ZnCl_2$) compared with those giving carbonium-ion polymerization of olefins (BF_3, $AlCl_3$, $SnCl_4$), the rapidity of the initiation, and the high yield of active centers. On the other hand, the energy of ion-pair formation can be greatly lowered in the presence of epoxide, since this will coordinate to a carbonium ion:



(II) (III)

with an estimated evolution of 80–100 kcal. mole^{-1}. The product can be described either as a coordinated carbonium ion (II) or an oxonium ion (III), and the former description is convenient when considering alternative ligands or the component terms of the energy of formation. It is reasonable to suppose that when such coordinate stabilization energy is available, ion-pairs may be formed rapidly by comparatively weak Lewis acids, and will be much less reactive than carbonium ions.

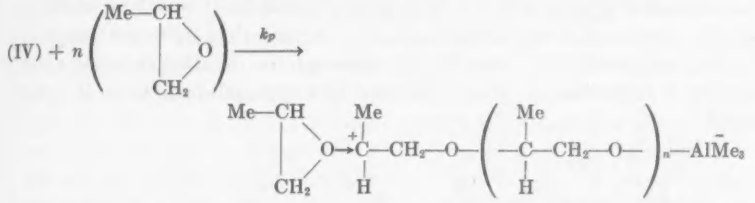
We conclude, therefore, that $AlMe_3$ can form ion-pairs rapidly in the presence of epoxide, and that the essential prerequisite in this reaction is the collision of (I) with a second epoxide molecule, whose function is to stabilize the cation formed. Thus the initiation step would comprise the formation of (I) followed by:



(I) (IV)

to form the active center (IV). The monomer molecule stabilizing the cation may be replaced by an oxygen atom forming part of a polymer chain when polymer has been formed. This leads to cyclization during the propagation step, and is also considered to affect the initiation of the stereoregulating centers in the secondary wet reaction.

Propagation will follow by the further reaction of IV with epoxide:



This should not be taken to imply that the cation and counteranion become widely separated; this is unlikely because of the electrostatic energy term involved. The production of low cyclic polymers indicates that the growing chain forms a loop in which the monomer coordinating the positive ion is easily exchanged for an oxygen atom in the polymer chain,[6] probably that attached to Al, since the negative charge on the counteranion will be associated with it. This constitutes a transfer rather than a termination reaction, since the $AlMe_3$ is unchanged, and initiation is very fast.

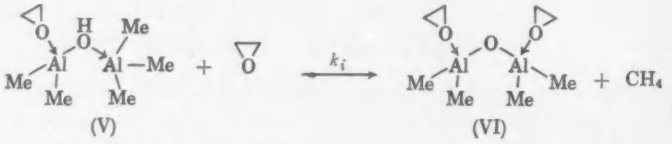
In view of the relative stability of the oxonium ion, there is no reason to suppose that a cationic reaction in epoxide systems should show a low or negative activation energy, which in vinyl polymerization is a reflection of the great activity of unstabilized carbonium ions. Again in contrast to the carbonium reaction, the dielectric constant of the medium may have little proportional effect on a concentration of stable ions approaching the limiting catalyst concentration, especially since the counteranion and cation are joined through the polymer chain, restricting the intervention of the dielectric.

The termination of the active center must involve the recombination of charges, and the evolution of methane suggests that this happens by combination of a methyl group on the anion with a hydrogen ion abstracted from the cation, leaving the polymer chain, containing an olefinic group, attached to the aluminum atom. This chain may be very short, because of the rapid transfer reaction. However, both the kinetic results and the stoichiometry of gas evolution show that the mechanism of this process is complicated, involving collision with another catalyst species, and that ultimately only one in four Al atoms produce an active center. Our formulation of the initiation reaction may therefore be oversimplified (e.g., it may involve a dimeric rather than a monomeric catalyst species), but since we have as yet no information on its kinetics, a more detailed explanation must await further experiment. Nevertheless, the evidence on the reaction as a whole supports the view that the active center is cationic.

The Primary Wet Reaction

For this reaction we have earlier postulated the initial rapid formation of a species Al_2Me_5OH, which undergoes a slower reaction (velocity constant k_i) involving the epoxide, to give the active catalyst. We assume that compounds of the type Al_2Me_5OH are coordinated by epoxide to give the

metal atoms a coordination number of at least four, which must be maintained in any further reaction. This gives (V) as a likely structure, and from the kinetics and the evolution of gas, we conclude that the overall reaction corresponds to the formation of (VI), although the detailed function of the epoxide is uncertain in view of the effect of ether and dioxane on the reaction:



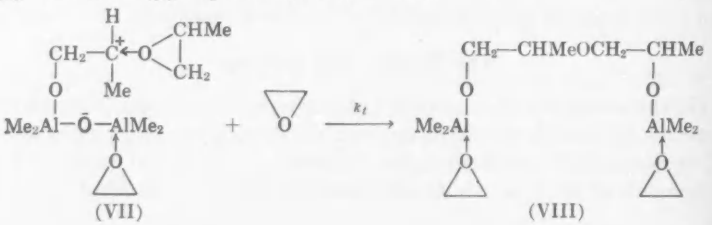
(V) (VI)

The Al atoms in (VI) should be more electronegative than that of $AlMe_3$, because of the bond to oxygen, and consequently should form cations even more readily, so that (VI) is a plausible initiating species. Since the initiation in the dry reaction is rapid, initiation by (VI) will be even more so, and k_i will therefore determine the overall rate of initiation.

In propagation, the cationic active center can obviously undergo the same exchange of ligands leading to cyclization postulated for the dry reaction, and the similarity of the products supports a uniform interpretation of the two centers. The value of k_p obtained for the propagation step need not necessarily be the same for the dry and primary wet reactions, since the cationic center may be influenced by the proximity of the counteranion. The stoichiometry of the methane evolution in the dry reaction suggests that the active center may have a large counteranion involving four Al atoms, and the value of the propagation constant for the dry reaction estimated on this assumption is lower than that for the wet reaction by a factor of ten. The attribution of this difference to the effect of the counteranion receives some support from the similar difference between the termination constants, which certainly depend on the nature of the counteranion.

The effect of ether and dioxane on the rate of propagation appears as a natural consequence of their replacing the epoxide as coordinating stabilizer of the cation. The oxonium ion formed cannot propagate until exchange with the epoxide occurs again, and the concentration of effective active centers will be reduced.

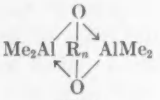
The termination reaction does not involve the loss of a further methyl group, and must therefore take place by combination of the cation with the oxygen-containing group on the counteranion:



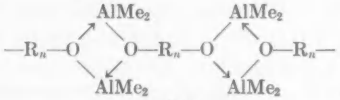
(VII) (VIII)

On hydrolysis, (VIII) should give a short polymer chain (2-4 units) containing two —OH endgroups, which is consistent with the higher —OH content found in the products compared with those of the dry reaction. The increased value of k_t compared with that of the dry reaction is again consistent with the nature of the counteranions in the two reactions. In the dry reaction (IV), the negative charge is spread over the sp^3 hybrid orbitals of the metal atom, with an increased probability of localization on the electronegative oxygen atom connecting the metal atom with the growing polymer chain. This leads to cyclization by intermittent interaction of the cation with this oxygen atom; a reaction which will take place much more frequently than that with the less electronegative methyl groups in termination. In (VII), however, the oxygen atom joining the Al atoms will compete with that of the polymer chain in localizing the negative charge, and will therefore have a higher probability of terminating the cation than the methyl groups. This localization would account both for exclusive termination by the oxygen-containing group, and for the larger value of k_t.

The postulation of (VIII) as an inactive species contains an apparent paradox, in that the arguments advanced to support the catalytic activity of (VI) must apply equally to (VIII), where each Al atom also has a bond to oxygen which will increase its electronegativity relative to that of $AlMe_3$. However, the formation of an active cation necessarily involves the epoxide as a coordinating ligand, and we suggest that this is largely prevented in (VIII) by the preferential coordination of oxygen atoms joining Al to the polymer chain. This may be intramolecular (IX) or intermolecular (X).



(IX)



(X)

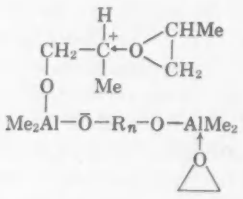
where R_n represents a polymer chain of n units.

The work of Bradley et al.[8] suggests that complex formation of this type is not affect by the length of R_n, but is prevented by steric hindrance when the atom in R_n adjacent to the bridging oxygen atom is highly substituted (e.g., tertiary). Thus (VI), in contrast to (VIII), would be unable to form such complexes, and would therefore be an active catalyst. The deactivation of (VIII) by complex formation, even in the presence of epoxide, is supported by recent work[3] on the complexity of $Me_2Al—O—CH_2CH_3$, which is found to be dimeric in hexane solution in the presence of propylene oxide, and is a very weak catalyst, giving a slower rate of polymerization than the secondary wet reaction. Qualitative observations on the viscosity of the reaction mixture at the end of the primary wet reaction indicate that it is more viscous than would be expected from the molecular weight of the polymer obtained on hydrolysis, and this would be consistent with the formation of the intermolecular complex (X).

Although most of (VIII) may be deactivated in forming (IX) or (X), the presence of epoxide as an alternative ligand will give an equilibrium, so that some of (VIII) will remain as such, even if only in very small concentration. This should therefore give further polymerization, although at a much reduced rate, and may thus be considered as a possible active species for the secondary wet reaction.

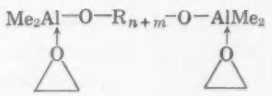
The Secondary Wet Reaction

The hypothesis that the active species in this reaction is a small concentration of (VIII) in equilibrium with inactive (IX) or (X) is consistent with both the low rate and the face that only approximately 10^{-3} of the total Al present is effective. The production of high molecular weight polymer and the apparent absence of a termination reaction seem at first sight to be incompatible with a cationic center, but on applying the rationale developed in the previous section, they appear as a logical outcome of the catalyst species postulated. Assuming that a cationic center is formed by one of the Al atoms in (VIII), e.g.:



(XI)

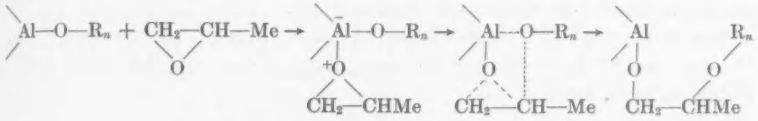
propagation will follow in the normal way, and termination will occur, as in (VII → VIII) and for the same reasons, by combination of the cation with the oxygen-containing group on the counteranion. If m monomer units are added during propagation, the termination reaction gives:



which, for purposes of initiation, is identical with (VIII), and the process can recur indefinitely with an ever-increasing length of polymer chain between the two Al atoms. Thus, the repeated process of cationic initiation, propagation and termination will give the overall effect of a nonterminated high molecular weight polymerization. Some low cyclic polymer will also be produced, but since the concentration of (VIII) is very small, this would be difficult to distinguish quantitatively from the products of the primary wet reaction already present.

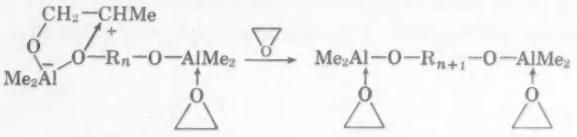
The apparent absence of termination has previously led to the classification of the mechanism in this type of reaction as "coordinate,,[5,9] or "coordinate anionic".[10] This envisages the initial coordination of the epoxide

to the metal atom, followed by attack of the anionic —O—R_n group to give a stepwise addition:



In this sequence, which involves a polarization of charge rather than the formation of a true ion pair, the rate-determining step is the initial coordination of epoxide, and steric factors affecting this step are invoked to explain the production of regular polymer.

We consider, on the contrary, that the Al atoms in solution must always have a coordination number of at least four, and that the rate-determining step is therefore not the initial coordination of epoxide (since (VIII) would not exist unless such coordination were already *in situ*), but rather the rate of formation of an ion-pair. This depends on the possibility of solvating the incipient carbonium ion to give (XI), and normally involves the participation of a second monomer molecule. However, the two types of mechanism become formally similar if the incipient carbonium ion can be solvated by the —O—R_n group instead of by a second epoxide molecule. This would give (XII) instead of (XI), followed by immediate "termination," and the net effect is similar to the coordinate mechanism:



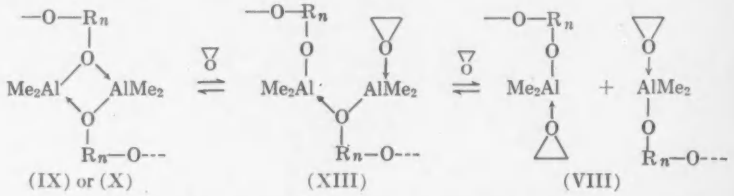
(XII)

Nevertheless, the basic difference would still remain, viz., that the rate-determining step and steric factors affecting it would involve solvation of the cation by the —O—R_n group, rather than the initial coordination of epoxide. In fact, however, the use of models shows that solvation by the —O—R_n group is unlikely when it is attached to the same Al atom as the coordinated epoxide (since this would involve a five-membered ring), but is favored when the epoxide and the —O—R_n group are on adjacent Al atoms. When this can happen, the solvation energy obtained, and hence the change of forming an ion-pair, depends upon the steric interaction of substituents on the incipient cation with those of R_n, and we envisage this as the basic factor in the stereoregulating process.

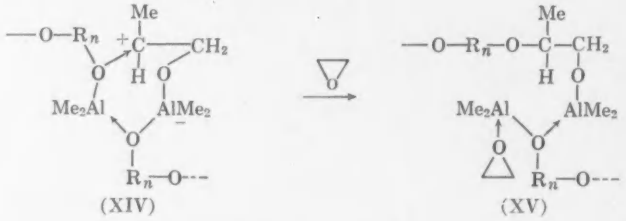
With (VIII), however, this does not arise, and since there is no effective steric hindrance to either optical configuration of propylene oxide in solvating the cation (XI), we conclude that this catalyst species will give random addition and therefore produce only amorphous polymer. Vandenberg[11] has suggested that with *trans*-2,3-epoxybutane as monomer, even simple cationic propagation is stereospecific, and postulates a significant

difference in the solvation energy of the two optical configurations towards the corresponding carbonium ion. This would account for the much higher yield of crystalline polymer from this monomer.

In addition to (VIII), there will also be present in very small concentration the species (XIII) as the intermediate stage in the equilibrium between (VIII) and (IX) or (X):



This species (XIII) is thought to be the catalyst responsible for the stereoregular sequences in the polymer. The epoxide molecule in (XIII) has the same potentialities for cation formation as those in (VIII), but this is unlikely to occur in the same way (viz., by collision with a second epoxide molecule), since the bridging oxygen atom displaced by the epoxide is immediately adjacent as a potential source of coordinate stabilization for the cation, and will form the transition state (XIV). Here, however, the negative charge has a path around the ring to the cation, and "termination" will be very rapid, either by collision with epoxide to form (XV), (in which case the process is repeated), or by the re-formation of (IX) or (X):



As before, the process can repeat itself indefinitely to give high polymer, and the rate-determining step will be the rate of formation of the cation, which will depend on the energy of the transition state (XIV). Since the major energy term involved is that due to coordinate stabilization of the cation, any steric interaction between groups on the epoxide and the polymer chain which affect this term will affect the reaction rate exponentially. Briefly, then, there is a basis here for steric selection, since for a given configuration of the polymer chain adjacent to the coordinating oxygen atom, the *d*- and *l*-configurations of propylene oxide will give differing energies for the transition state (XIV), and hence different rates of addition. The use of models shows that a series of such steps in succession will give a stereoregular sequence in the polymer chain.

We conclude that although (XIII) is likely to be a stereoregulating catalyst, it cannot be exclusive in action, since although a given center has a higher probability of forming a sequence of units of one optical configuration than of the other, the latter will not be entirely excluded, leading to random inclusions. Rotation of the epoxide molecule in (XIV) about the metal–oxygen bond also gives an alternative transition state in which the ion is formed from a primary rather than a secondary carbon atom. This will have a higher energy of formation than the latter case, due to the loss of the inductive stabilization of the methyl group, but may compete with ion-pair formation by the less favored configuration of the secondary carbon atom. This would lead to some head-to-head links in the polymer. Again, solvation of the cation by epoxide rather than the —O—R_n group (as in (XI)) will also give random inclusions, although the frequency factor for such a bimolecular solvation will be much lower than that for solvation by —O—R_n. These alternatives will give small random inclusions in mainly stereoregular sequences, but the principal cause of long random sequences will be the exchange of the catalyst between its alternative forms of (VIII) and (XIII). Thus, a growing —O—R_n chain may at different times form part of (VIII) (random addition) or (XIII) (mainly regular addition), and will therefore have the block copolymer structure of random and regular sequences found in practice.

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Synopsis

The polymerization of propylene oxide at 0°C. in dichloromethane solution, catalyzed by trimethyl aluminum, has been investigated kinetically both in the presence of catalytic amounts of water, and under rigorously dry conditions, using a vacuum technique and dilatometry. In the absence of water, a catalytic species, believed to be an oxonium ion-pair, is formed very rapidly and adds further propylene oxide to form cyclic polymer of low molecular weight ($\approx$250). The active species terminates by a reaction which is essentially first-order, and at low catalyst concentrations the polymerization stops before all of the monomer has been consumed. During the reaction, methane is evolved, and the stoichiometry of gas evolution indicates that four aluminum atoms are involved in the active center. The rate constant for the termination reaction has been determined, and that for propagation estimated. In the presence of catalytic amounts of water, methane is rapidly evolved before polymerization starts, corresponding to the formation of Al_2Me_5OH. This undergoes a slower initiation reaction during which the

active catalyst is formed, again evolving methane in quantity corresponding to the formation of $Me_2Al—O—AlMe_2$. This catalyst gives a faster rate of polymerization than that of the dry reaction, but also terminates more rapidly without further loss of methyl groups from the metal atom. The active center is again thought to be an oxonium ion-pair, and the initial stage of the reaction gives polymer almost identical with that produced in the dry reaction. Unlike the latter, however, this initial stage is followed by a further slow polymerization in the presence of excess propylene oxide, which gives high molecular weight ($\approx 10^6$) partly stereoregular polymer. The catalyst for this second slow stage is formed in the termination of the catalyst species of the first stage, and its probable nature is discussed. Provided that the molar ratio of water to aluminum is less than 1:1, the reaction is homogeneous throughout, with a maximum initial rate at a ratio of 0.5:1. At ratios greater than 1:1, the rates of both stages are reduced, and the reaction mixture becomes heterogeneous. The rate constants for the propagation and termination reactions in the first stage of the wet reaction have been measured, and the rate constant for the initiation reaction estimated. The effect of adding dioxane or diethyl ether, which reduce the rate of polymerization, has been studied quantitatively. Earlier kinetic results obtained at 80°C. are reinterpreted, and mechanisms are proposed for the various stages of the reaction.

Résumé

On a étudié la cinétique de polymérisation de l'oxyde de propylène à 0°C en solution dans le dichlorométhane, initiée par le triméthyl-aluminum en présence de quantités catalytiques d'eau et dans des conditions rigoureuses d'absence d'eau, utilisant la technique du vide et la dilatométrie. En absence d'eau, l'espèce catalytique, que l'on suppose être une paire d'ion oxonium, se forme rapidement et s'additionne rapidement l'oxyde de propylène pour former un polymère cyclique de bas poids moléculaire (≈ 250) Les espèces actives subissent la désactivation par une réaction qui est essentiellement du premier ordre et à faible concentration en catalyseur la polymérisation s'arrête avant que tout le monomère n'ait été consommé. Au cours de la réaction, on forme du méthane et la stoéchiométrie de l'apparition du gaz indique que quatre atomes sont inclus dans le centre actif. On a déterminé les constantes de vitesses de la réaction de terminaison et on a évalué la constante de propagation. En présence de quantités catalytiques d'eau, le méthane est rapidement formé avant le début de la polymérisation ce qui correspont à la formation d'Al_2Me_5OH. Celui-ci subit une réaction d'initiation plus lente au cours de laquelle le catalyseur actif est formé en même temps que du méthane en quantité correspondant à la formation de $Me_2Al—O—AlMe_2$. Ce catalyseur donne une vitesse de polymérisation plus grande que celle de la réaction en l'absence d'eau, mais termine aussi plus rapidement sans expulsion ultérieure de groupement méthyle de l'atome métallique. Le centre actif est alors supposé être une paire d'ions oxonium, et l'étape d'initiation de la réaction donne un polymère identique à celui produit par la réaction sans eau. Non-obstant cela, cette étape initiale est suivie d'une polymérisation ultérieure et lente en présence d'un excès d'oxyde de propylène qui donne un polymère de haut poids moléculaire ($\approx 10^6$) et partiellement stéréorégulier. Le catalyseur de cette seconde étape lente est formé par la terminaison de l'espèce catalytique de la première étape et on discute sa nature probable. Pour autant que le rapport molaire de l'eau et de l'aluminium soit inférieur à 1/1, la réaction sera homogène, avec une vitesse initiale maximum pour un rapport de 0.5/1. Pour des rapports supérieurs à 1/1, les vitesses de deux étapes sont réduites et le mélange réactionnel devient hétérogène. Les constantes de vitesse de réaction de propagation et de terminaison pour la première étape de la réaction en présence d'eau, ont été mesurées et on a estimé la constante de vitesse pour la réaction d'initiation. Les effets dûs à l'addition de dioxanne et d'éther diéthylique qui reduisent considérablement la vitesse de polymérisation, ont été étudiés quantitativement. Des résultats cinétiques antérieurs obtenus a 80°C sont réinterprêtés et on propose des mécanismes relatifs aux différentes étapes de la réaction.

Zusammenfassung

Die Kinetik der durch Aluminiumtrimethyl katalysierten Polymerisation von Propylenoxyd bei 0° in Dichlormethanlösung wurde in Gegenwart katalytischer Mengen Wasser und unter strengem Wasserausschluss dilatometrisch nach einer Vakuummethode untersucht. In Abwesenheit von Wasser wird sehr rasch eine katalytisch wirkende, als Oxoniumionen-Paar angenommene Substanz gebildet, die weiter Propylenoxyd unter Bildung eines cyclischen, niedermolekularen Polymeren ($M \approx 250$) addiert. Die aktiven Zentren zeigen Kettenabbruch durch eine Reaktion im wesentlichen von erster Ordnung und bei niedriger Katalysatorkonzentration kommt die Polymerisation vor dem vollständigen Monomerverbrauch zum Stillstand. Während der Reaktion wird Methan entwickelt und die Stöchiometrie der Gasentwicklung spricht für die Teilnahme von vier Aluminumatomen an einem aktiven Zentrum. Die Geschwindigkeitskonstante der Abbruchsreaktion wurde bestimmt und die des Wachstums abgeschätzt. In Gegenwart katalytischer Wassermengen wird vor dem Polymerisationsbeginn rasch das der Bildung von Al_2Me_5OH entsprechende Methan entwickelt. Al_2Me_5OH liefert eine langsamere Startreaktion, während welcher sich der aktive Katalysator bildet und wobei wieder eine der Bildung von $Me_2Al—O—AlMe_2$ entsprechende Methanmenge entwickelt wird. Dieser Katalysator liefert eine höhere Polymerisationsgeschwindigkeit als derjenige der "trockenen" Reaktion, zeigt aber auch einen rascheren Abruch ohne weiteren Methylgruppenverlust von Metallatom. Als aktives Zentrum wird wieder ein Oxoniumionen-Paar angenommen; die Anfangsphase der Reaktion liefert eine mit dem bei der "trockenen" Reaktion gebildeten fast identisches Polymeres. Zum Unterschied folgt aber hier auf die Anfangsphase eine weitere langsame Polymerisation in Gegenwart von überschüssigem Propylenoxyd, welche ein hochmolekulares ($\approx 10^6$), zum Teil stereoreguläres Polymeres liefert. Der Katalysator für diese zweite langsame Phase wird beim Abbruch des Katalysators der ersten Phase gebildet; seine wahrscheinliche Natur wird diskutiert. Bei einem Molverhältnis Wasser zu Aluminium kleiner als 1:1 ist die Reaktion in ihrem ganzen Verlauf homogen, mit einem Maximum der Anfangsgeschwindigkeit bei einem Verhältnis 0,5:1. Bei einem Verhältnis grösser als 1:1 wird die Geschwindigkeit in beiden Reaktionsphasen herabgesetzt und das Reaktionsgemisch wird heterogen. Die Geschwindigkeitskonstanten der Wachstums- und Abbruchsreaktion in der ersten Phase der "nassen" Reaktion wurden bestimmt und die Geschwindigkeitskonstante der Startreaktion abgeschätzt. Der Einfluss von zugesetztem Dioxan oder Diäthyläther, die beide die Polymerisationsgeschwindigkeit herabsetzen, wurde quantitativ untersucht. Frühere, bei 80° erhaltene kinetische Ergebnisse werden neu interpretiert und Mechanismen für die verschiedenen Reaktionsphasen vorgeschlagen.

Discussion

G. Smets (*Louvain, Belgique*): Is there any influence of the degree of conversion on the rate of reaction from the point of view of the "dry" reaction or your "wet" reaction?

R. C. Colclough: The polymer yield of the primary reaction in the absence of co-catalyst is a function of the initial concentration of active centers, the propagation constant, and the termination constant

$$[M_0] - [M_p] = (k_p/k_t)\,[C_{0_p}]$$

Of these, we have as yet explicitly determined only the termination constant. In the primary wet reaction, the simple relation given above is complicated by the relatively slow production of active centers (initiation reaction). We would not therefore expect any simple effect of co-catalyst on the yield of the primary reaction, since it will affect the number of active centers as well as the k_p and k_t values.

Empirically, we find that the yield of the primary reaction with $[H_2O]/[AlMe_3] = 0.5$ is slightly smaller than that of the corresponding dry reaction, but is attained much more rapidly, as indicated in our paper. We have not, in general, attempted to follow the secondary reaction for longer than about 300 hr., but from a few experiments in which the reaction time was extended to a month, we conclude that the secondary reaction is probably limited only by the disappearance of monomer.

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Stereospecific Polymerization of Methyl Methacrylate by Means of Tertiary Alcoholates

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A great quantity of data on the anionic polymerization of methyl methacrylate has been compiled. Much attention has been given to the polymerization of methyl methacrylate by means of lithium compounds and Grignard reagents as well as to the dependencies connected with the structure of the polymer formed. The study of the polymerization is, however, from the kinetic point of view, accompanied by difficulties caused by the rapid polymerization process, which is difficult to control, and by the reaction of the initiators with the conjugate system C=C—C=O of the ester in various ways. Therefore, relatively few data on the polymerization mechanism are available.[1–8,14]

To get a more precise knowledge of the polymerization process it is necessary to discover those initiators which do not interfere with the initiation and growth process. The analysis of the reaction of BuLi with conjugate esters[9] shows that tertiary lithium alcoholate is capable of initiation. Substances of this type are well known in organic chemistry as good condensation agents. The polymerization product is a stereoregular polymer, as in the case of polymerization with BuLi. Lithium compounds are suitable for initiation because the growing lithium polymethyl methacrylate anion is sufficiently reactive to polymerization, relatively stable to side reactions, and maintains its life even at elevated temperatures. Polymerizations with lithium *tert*-butoxide are very satisfactory, high conversions being attained at low initiator concentration with suitable experimental rates. The higher alcoholates of lithium are more advantageous because they are more soluble at high conversions. Results of the polymerization kinetics and the characterization of the polymer prepared with the Li alcoholate of 1,1-dimethylbutanol-1 (*tert*-hexanol) as the initiator are given in this paper.

EXPERIMENTAL

The polymerization was followed dilatometrically in the temperature range of 0–30°C. Polymerizations in ampules were carried out orientatively in the −40 to 30°C. range. All materials used for the polymerization were prepared and kept in an argon atmosphere. The methyl meth-

acrylate (commercial Czechoslovak product) was repeatedly shaken with dilute alkali, dried, and twice distilled on a 20-plate column. Before polymerization the methyl methacrylate was boiled for 2 hr. with Na under reduced pressure and then redistilled. Its purity was checked by means of gas chromatography.

1,1-Dimethylbutanol-1 (*tert*-hexanol) was prepared by the reaction of ethyl butyrate with methylmagnesium iodide. The tertiary alcohol resulting from the reactions was thoroughly rectified by double distillation on a 10-plate column (b.p. 121.5°C./738 mm. Hg). The purity was also checked by gas chromatography. The lithium alkoxide was prepared by heating the alcohol with a suspension of Li in benzene solution. The unreacted Li was filtered off, and the remaining traces of alcohol together with benzene were removed by distillation. The residue in the flask was purified by sublimation at 0.01 mm. Hg. The alcoholate forms on the walls of the flask a clear, glassy material, soluble in aromatic hydrocarbons. The purity of the alcoholate, determined by titration, was 99.9%.

Toluene (Lachema p.a.) was dried by Na and distilled. The dilatometers were filled in inert atmosphere. After addition of the monomer and the solvent (toluene), a solution of the alkoxide in toluene was added in the course of about 15 sec., the dilatometer was closed by a glass stopper and inserted into a thermostat. The results were reproducible to several per cent and were verified by independent series of experiments. The purity of the alkoxide seems to have the most important influence on the course of the polymerization. The conversion was determined by the precipitation and determination of the weight of the polymer obtained or calculated according to Schultz and Harborth.[10]

The time dependence of monomer consumption for various monomer concentrations up to a conversion of approximately 15% at 20°C., is shown

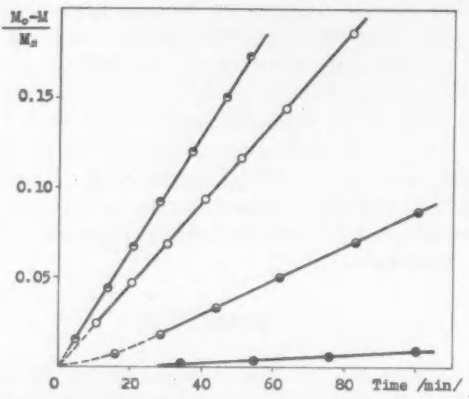


Fig. 1. Conversion of monomer as a function of concentration of methyl methacrylate: (●) 1.877 mole/l.; (◒) 3.747 mole/l.; (○) 5.615 mole/l.; (◓) 7.489 mole/l. [*tert*-HexOLi] = 0.05 mole/l.; temperature 20°C.

in Figure 1. The polymerization shows a linear dependence on the concentration of monomer in the range of concentrations of monomer and initiator studied up to about 60% (Figs. 2 and 3). At a higher conversion the rate decreases, but the polymerization reaches practically 100%. The rate of polymerization is third order with respect to monomer (Fig. 4). The dependence of the rate on the concentration of the initiator is shown in Figures 5–7. It is evident that the polymerization rate shows a linear dependence on the concentration of initiator [I] up to about 0.03 mole/l. At higher concentrations, the order, with respect to [I] decreases. At low

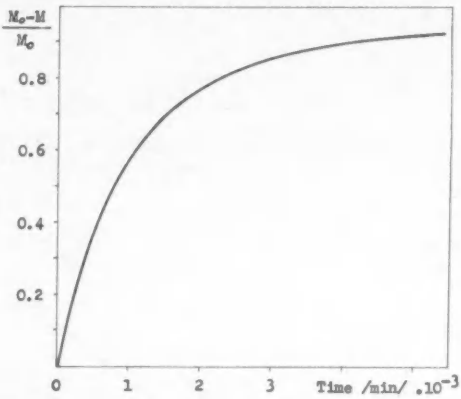


Fig. 2. Conversion of monomer as a function of time. [MMA] = 4.666 mole/l.; [*tert*-HexOLi] = 0.0200 mole/l.; temperature 20°C.

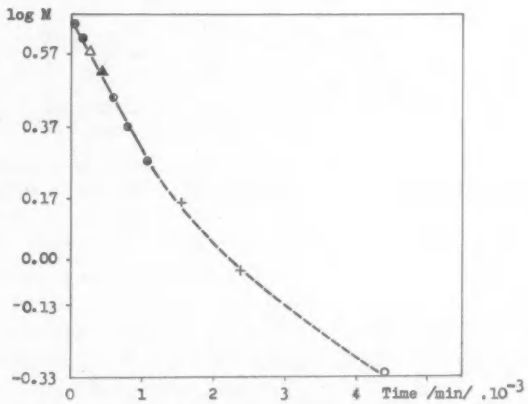


Fig. 3. Logarithmic plot of methyl methacrylate concentration vs. time: ( ) 4.67 mole/l.; (●) 4.20 mole/l.; (△) 3.73 mole/l.; (▲) 3.29 mole/l.; (◐) 2.80 mole/l.; (◑) 2.34 mole/l.; (◒) 1.87 mole/l.; (+) 1.40 mole/l.; (×) 0.934 mole/l.; (○) 0.467 mole/l. [*tert*-HexOLi] = 0.0200 mole/l.; temperature 20°C.

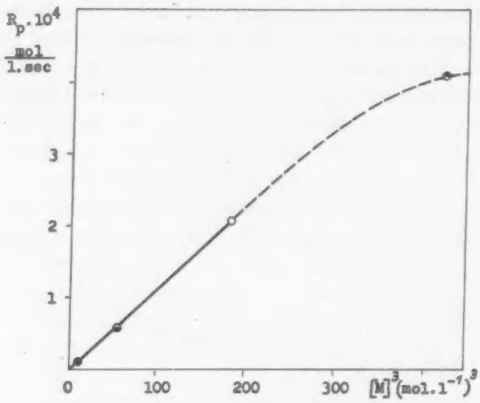


Fig. 4. Rate of polymerization vs. monomer concentration: (●) 1.877 mole/l.; (◒) 3.747 mole/l.; (○) 5.615 mole/l.; (◓) 7.489 mole/l. [*tert*-HexOLi] = 0.05 mole/l.; temperature 20°C.

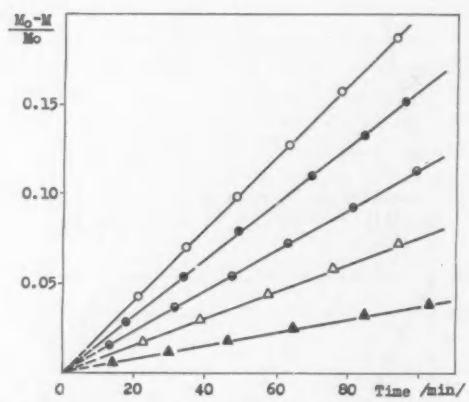


Fig. 5. Conversion of monomer as a function of Li *tert*-hexoxide concentration: (▲) 0.00987 mole/l.; (△) 0.0202 mole/l.; (◒) 0.0399 mole/l.; (●) 0.0751 mole/l.; (○) 0.1498 mole/l. [MMA] = 4.68 mole/l.; temperature 20°C.

monomer concentrations [M] or at low temperatures a short induction period occurs. It is not yet possible to say whether this period is related to the formation of the complex. The temperature dependence for the polymerization rate of a 50% solution for the 0–30°C. range is shown in Figure 8. The rise of the rate with the temperature from 0 to 20°C. is approximately regular. At a temperature higher than 20°C. the rate increases with a lower factor, which indicates a change of the course of some partial reaction during the polymerization. The polymers prepared at temperatures higher than 30°C. are of low molecular weight ($[\eta] < 1$).

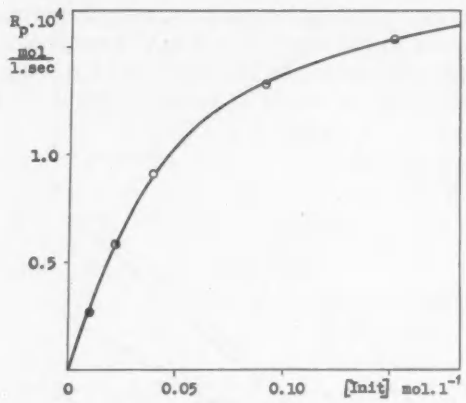


Fig. 6. Rate of polymerization vs. initiator (*tert*-HexOLi) concentration: (●) 0.00987 mole/l.; (◑) 0.0202 mole/l.; (○) 0.0399 mole/l.; (◓) 0.0751 mole/l.; (●) 0.1498 mole/l. [MMA] = 4.68 mole/l.; temperature 20°C.

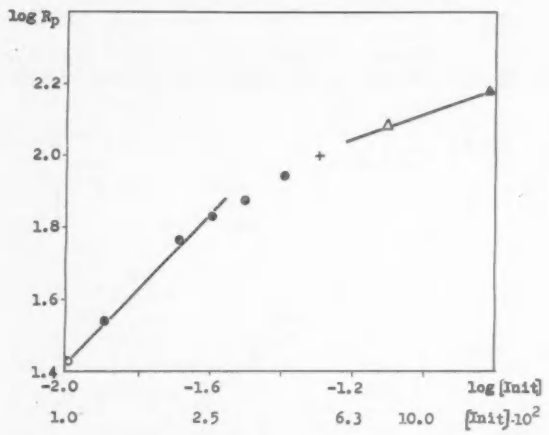


Fig. 7. Logarithmic plot of polymerization rate vs. initial concentration of *tert*-HexOLi: (○) 0.00987 mole/l.; (●) 0.0129 mole/l.; (◐) 0.0202 mole/l.; (◑) 0.0254 mole/l.; (◒) 0.0307 mole/l.; (◓) 0.0399 mole/l.; (×) 0.0501 mole/l.; (△) 0.0751 mole/l.; (▲) 0.1498 mole/l. [MMA] = 4.68 mole/l.; temperature 20°C.

The activation energy for the 0–20°C. range, calculated from the temperature dependence of the polymerization rate is 6.2 kcal./mole (Fig. 9). At temperatures higher than 0°C. and at higher conversions it is possible to observe the formation of a gel in a definite range of the concentrations of initiator and monomer. The gel is insoluble in all solvents as the result of a considerable branching of molecules in the course of the growth of polymer particles.

In comparison to the BuLi polymerization, the polymerization initiated with alkoxides is slower. It may be stated on this occasion, that polymerization of methyl methacrylate by the products of reaction of BuLi + methyl trimethylacetate (2:1 moles at normal temperature) which should

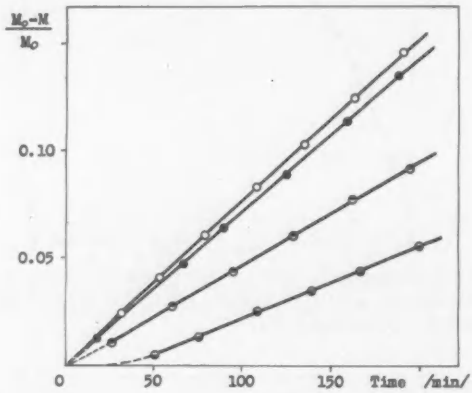


Fig. 8. Conversion of monomer as a function of temperature: (◒) 0°C.; (◓) 10°C. (●) 20°C.; (○) 30°C. [MMA] = 4.68 mole/l.; [*tert*-HexOLi] = 0.020 mole/l.

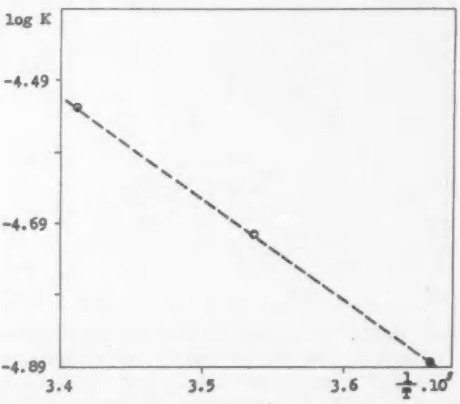


Fig. 9. Logarithmic plot of polymerization constant vs. temperature: (●) 0°C.; (○) 10°C.; (◒) 20°C. [MMA] = 4.68 mole/l.; *tert*-HexOLi] = 0.020 mole/l.

contain only the primary and the tertiary alkoxides, is faster even at −50°C. This disagreement is not yet fully explained. Either the reaction product contains undissociated reaction complex able to initiate, or the initiation is due to residual unreacted BuLi, which is stabilized by the alkoxide. In fact, in the mixture of BuLi with the alkoxide a new band

appears in the 1000–1100 cm.$^{-1}$ region, indicating the formation of a bond comparable with the hydrogen bridge. The decrease of reactivity of BuLi in alkoxide may be proved as well by the decrease of the heat of the reaction of BuLi, e.g., with a ketone.

Even if the decrease of reactivity is not substantial, it may enable better utilization of BuLi for polymerizations by limiting undesirable reactions.

A similar result is observed with a reaction product of BuLi and methyl isobutyrate. In this case, however, the metallation of isobutyrate can take place. The reactivity of the resulting Li α-isobutyrate may be expected to be similar to that of growing molecules.

Polymers prepared from solutions with a higher concentration than about 80% form slightly opalescent, hard blocks. The stereoregularity of polymers was determined by means of infrared spectroscopy in dioxane or chloroform solution and for insoluble products from the spectrum of films or more exactly by means of NSR spectroscopy.[11,12]

With all polymers prepared by means of initiation with tertiary alkoxide a band was observed corresponding only to isotactic polymer. The results are compiled in Table I.

TABLE I
Dependence of the Stereoregular Arrangement on Polymerization Conditions
(Solvent:Toluene, Ester: Methyl Trimethylacetate)

Sample number	Monomer concn. [M], %	Initiator	Temp., °C.	Conversion, %	Isotactic structure %
1	20	BuLi	−60	100	~95
2	20	BuLi	−50	18	~90
3	40	BuLi + ester	−50	75	100
4	20	BuLi + ester	−50	14	100
5	40	BuLi + ester	+20	18	95
6	90	*tert*-HexOLi	+20	100	100
7	20	*tert*-HexOLi	+20	100	100
8	50	*tert*-HexOLi	+20	19	~95
9	50	*tert*-HexOLi	+10	28	More than No. 8
10	50	*tert*-HexOLi	0	16	~95
11	83	*tert*-HexOLi	−10	11	100
12	83	*tert*-HexOLi	−20	7	100

In Table I the structure of polymers prepared by means of BuLi is compared to those prepared by alkoxide and the system BuLi plus methyl pivalate. It may be seen, that at a higher conversion the content of the isotatic structure decreases. The exact evaluation of the atactic or syndiotactic structure of the compared samples has not been carried out. The measurements were carried out by Ing. Schneider, Dr. Doskočilová, and Ing. Štokr of this Institute on a Zeiss type UR 10 spectrometer or a J. E. O. 60 Mcycles NSR spectrometer respectively.

RESULTS AND DISCUSSION

From the experimental section it is evident that Li alkoxides are suitable initiators for the experimental investigation of ionic methyl methacrylate polymerization. As is the case with low molecular chemistry, the participation of alkoxides in a reaction other than initiation is almost impossible. Unlike the case with alkyl lithium compounds, the primary reaction with the ester group is evidently not the most rapid reaction. The polymerization may comfortably be controlled even in the region of high monomer concentrations at temperatures over 0°C. The alkoxides are well defined compounds which may be prepared with a high degree of purity. In the solid state they are much less sensitive to manipulation than alkyl Li compounds. The polymerization proceeds regularly up to the highest conversions. At −40°C. the polymerization practically stops.

Summary of Results for Explanation of Mechanism

The consumption of the monomer in the medium range of concentration of methyl methacrylate is dependent on the first power of monomer up to conversions of about 70%. At higher conversions the polymerization slows down but continues to 100%.

The polymerization rate in diluted solutions is third order with respect to monomer and is first order with respect to initiator for initial conversions. At higher concentrations of initiator the order falls to the value of about 0.2.

From the relation of the temperature and the rate in the 0–20°C. range a value of $E_a = 6.2$ kcal./mole is obtained. At higher temperatures the rate increases with a lower factor.

Polymerization Mechanism

The polymerization rate corresponds to the equation

$$R_p = K[\mathrm{I}][\mathrm{M}]^3$$

Considering the consumption of the monomer to be a reaction of the first order we can assume that the growth takes place in centers, the number of which is proportional to $[\mathrm{I}][\mathrm{M}]^2$. These centers must be formed at the beginning of the polymerization by a more rapid reaction before the consumption of the monomer by the polymerization takes place. Simultaneously, the assumption must be valid that during polymerization no decrease of the growing chains occurs, i.e., that no termination, but only transfer (by monomer) is possible.

Initiation:

$$\mathrm{ROLi} + 2\mathrm{M} \rightarrow [\mathrm{complex}]^{-}\mathrm{Li}$$

Propagation:

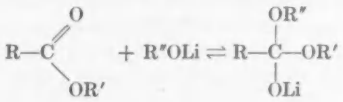
$$[\mathrm{complex}]^{-}\mathrm{Li} + \mathrm{M} \rightarrow \mathrm{M}^{-}\mathrm{Li}$$

Transfer:

$$-M^-Li + M \rightarrow -M + M^-Li$$

In the reactions of alkoxides with the monomer, the 1,2 and 1,4 additions can probably occur more easily than the 3,4 addition, because in the latter case a much stronger base than the initial compound would be formed. As a result of such reaction in this first phase of the initiation, the equilibrium would be considerably displaced in the direction of the alkoxide. This equilibrium would also mean the dependence on the momentary concentration of monomer during the polymerization.

A further reaction which may have a greater importance is the addition of the alkoxide to the ester group (i.e., the 1,2 addition). This reaction in fact represents the basic alcoholysis of ester:



For unsaturated esters this reaction may be complicated by formation of a complex by 1,4 addition. With small quantities of alkoxide this addition may proceed rapidly. By further addition of the monomer the complex may become stabilized and form centers of growth. The fact that the polymer prepared by polymerization to low conversions is practically pure isotactic polymethyl methacrylate, supports the complex character of the polymerization. A similar mechanism occurs (at least in part) in the polymerization initiated by organolithium compounds which form a complex with the products of the reaction with the ester group.

During the initiation by the alkoxide, the polymerization proceeds according to concentration of the initiator practically up to a conversion of 100%. This may take as long as a week, indicating that the growing chain is relatively unreactive. This idea is supported by low molecular analogs as well, for instance by comparison with the stability of α-Li methylisobutyrate to self-condensation reactions.[13] All the facts indicate the suitability of Li compounds for the initiation of methyl methacrylate polymerization. The compounds of Na and K are stronger bases and, unlike Li compounds, generally react with the conjugated system C=C—C=O, mostly by the addition on the carbonyl group. In agreement with the general behavior of organic lithium compounds it is, however, necessary to consider a similar reaction of the growing chain as well. The fact that the polymerization proceeds up to 70% conversion as a reaction of the first order indicates that such a reaction with the monomer either does not take place at all or has the character of a transfer. In the first case the molecular weight would increase indefinitely without dependence on other conditions with the exception of temperature. Kinetically measurable termination by means of the Dieckmann condensation would take place from a definite temperature. In the second case the molecular weight

would depend on the concentrations of initiator and monomer. The experimental results are in agreement with the second assumption. During rapid polymerizations (which proceed according to the same mechanism as the slow ones) products with $[\eta] < 1$ are formed. Although $[\eta]$ increases with increasing conversion, an insoluble compound (gel) is also formed as a result of a condensation reaction with the ester group of the polymer. The assumption of a transfer by the mechanism stated is not in contradiction with the suggested initiation mechanism. Evident branching complicates the correlation of kinetic results with the molecular weight. The prepared gels swell considerably indicating a thin, three-dimensional structure. Temperature is the decisive factor for the formation of the gel.

The stereoregular arrangement depends less on the conversion than is the case for initiation with Grignard reagents.[14] The structure of the insoluble fraction, which represents the average composition at a high conversion, is equally isotactic as the extract or polymer at initial conversion.

The isotactic component varies somewhat with decreasing temperature. A slight variation of the stereoregular component with the temperature (if it takes place at all) may be observed.

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Synopsis

The kinetics of the polymerization of methyl methacrylate by means of tertiary lithium alkoxide were studied in the range of 0–30°C. The polymerization rate is first order with respect to [I] and third order with respect to [M]. The activation energy is 6.2 kcal./mole. The progress of the conversion with time corresponds to a first order reaction to [M] up to a 70% conversion. The structure of the polymer is isotactic up to highest conversion with a slight dependence on temperature in the range. The polymerization of methyl methacrylate initiated by an alcoholate represents a process with well defined initiation conditions, probably proceeding without side reactions of the initiator.

Résumé

On a étudié la cinétique de la polymérisation du méthacrylate de méthyle par le *tert*-alcoolate de Li dans des limites de 0°C jusqu'a +30°C. La vitesse de la polymérisation est de 3ème ordre par rapport à [M] et de 1er ordre à [I]. L'énergie d'activation globale est 6.2 kcal/mole. Le degré d'avancement en fonction du temps correspond à une réaction du 1er ordre par rapport à[M]justqu'à une conversion de 70%. La structure du polymère à une conversion est isotactique avec une légère dépendance de la température. La polymérisation du méthacrylate de méthyle initiée par un alcoolate représente un procédé pur dans des conditions d'initiation bien définies, probablement sand réactions secondaires en ce qui concerne l'initiateur.

Zusammenfassung

Es wurde die Kinetik der Polymerisation von Methylmethacrylat in Gegenwart von tertiärem Li-Alkoholat im Bereich von 0°C bis 30°C untersucht. Die Polymerisationsgeschwindigkeit ist von dritter Ordnung in bezug auf[M] und von erster Ordnung in bezug auf[I] Die Bruttoaktivierungsenergie beträgt 6,2 kcal/Mol. Die Zeitabhängigkeit des Umsatzes entspricht bis zu 70% Umsatz einer Reaktion erster Ordnung in bezug auf [M]. Das Polymere besitzt Umsatz isotaktische Struktur mit schwacher Temperaturabhängigkeit. Die Polymerisation von Methylmethacrylat bei Start durch ein Alkoholat zeichnet sich durch gut definierte Startbedingungen, wahrscheinlich ohne Sekundärereaktionen des Starters, aus.

Discussion

H. W. Schnecko (*Mainz, Germany*): How is it possible to determine the tacticity by NMR? You should have overlapping with methyl H-atoms of the initiating alkoxide.

D. Lím: The stereoregularity of our polymers was compared with mixtures containing a known quantity of syndiotactic polymer, the tetramethylsilane being used as a reference substance. No disturbing effect was observed.

B. Eroussalimsky (*Léningrad, U.R.S.S.*): Have you some data about the dependence of the molecular weight of polymer on the polymerization time?

D. Lím: At present the molecular weights of our polymers cannot be safely determined owing to the parallel branching and transfer reactions.

T. Tsuruta (*Kyoto University, Japan*): Do you have some experimental results for solvent effect? How about tetrahydrofuran as the solvent for the polymerization? I think polar solvent favors the formation of syndiotactic structure.

D. Lím: In the introduction I said that we tried at first to find as simple systems of complex anionic polymerization as possible. The presence of tetrahydrofuran would mean at least a three-component system with far more possibilities of the initiating effect. Another reason of the absence of ethers in the present state of our research was the possible stability complication of the growing chains similary as in the case of *t*-BuLi the presence of ethers.

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On the Two-State Mechanism for Homogeneous Ionic Polymerization

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1. Preface

To explain the occasional occurrence of "stereoblock" structures in homogeneous[1] anionic polymerization of α-olefins we recently proposed that in these polymerizations the reactive end of a growing polymer can have several, say N, states $\{1\}, \{2\}, \ldots, \{N\}$ which are in dynamic equilibrium and that each such state is capable of adding monomer with its own rate and stereospecificity. In the absence of quantitative experimental evidence to the contrary, it appears that for the present it is expedient to take advantage of the reduction in the number of free parameters which results when $N = 2$, and to consider in detail the consequences of a two-state mechanism. Indeed, most of the interesting qualitative features of the multistate mechanism are already present in the two-state case. Here we summarize those theoretical results on the two-state model which appear to us to be accessible to experimentation. The emphasis here is on the diastereosequence and molecular weight distributions. Of course, to illustrate the effect on these distributions of the presence of two polymerizing species in dynamic equilibrium, it is not necessary to specify the detailed chemical structures of the species.

2. Chemical Hypotheses

We use here the notation of Fox and Coleman.[2,3] Consider a poly-α-olefin molecule and number the asymmetric carbon atoms of its principal chain in the order in which they were added during polymerization. If the mth and $(m + 1)$th asymmetric chain atoms have the same stereoconfiguration, then we say that the mth placement is isotactic; if these two asymmetric atoms have opposite stereoconfigurations, then we say that the mth placement is syndiotactic. Note that one placement involves two monomer units. A diastereosequence of length k is an ordered set of k adjacent placements, say, the mth, $(m + 1)$th, $\ldots$, $(m + n - 1)$th placements which express, respectively, the stereorelationship between the mth and $(m + 1)$th, the $(m + 1)$th and $(m + 2)$th, $\ldots$, the $(m + n - 1)$th and the $(m + n)$th asymmetric chain atoms.

The polymerizations which we consider here are idealized in that we assume instantaneous initiation, no irreversible termination, and no chain transfer or depolymerization. We assume that the diastereosequences generated in the states $\{1\}$ and $\{2\}$ are free from penultimate effects, i.e. are Bernoullian in the sense in which the term is used in references 2 and 3. Of course, when reactions $\{1\} \rightleftharpoons \{2\}$ are not instantaneously fast when compared with the addition reactions, the diastereosequence distribution of the resulting polymer will be non-Bernoullian; in fact, it will be non-Markoffian.[3,4]

We indicate the condition of a polymer molecule by the symbol E_x^n. The superscript n represents the degree of polymerization, and $x = 1$ if the reactive end is in state $\{1\}$ while $x = 2$ for the state $\{2\}$. Denoting the monomer by M we can write the six basic chemical reactions of the two-state mechanism as follows:

$$E_1^n \xrightarrow{\lambda_b} E_2^n \tag{1a}$$

$$E_2^n \xrightarrow{\lambda_a} E_1^n \tag{1b}$$

$$E_1^n + M \xrightarrow{k_{1,i}} E_1^{n+1} \tag{1c}$$

$$E_1^n + M \xrightarrow{k_{1,s}} E_1^{n+1} \tag{1d}$$

$$E_2^n + M \xrightarrow{k_{2,i}} E_2^{n+1} \tag{1e}$$

$$E_2^n + M \xrightarrow{k_{2,s}} E_2^{n+1} \tag{1f}$$

Here λ_b is a rate coefficient for that reaction which takes a growing chain from state $\{1\}$ to state $\{2\}$. In other words, the probability that a polymer molecule, known to be in the state $\{1\}$ at the time t, goes to the state $\{2\}$, i.e., makes a transition of type 1a, in a time interval dt at t is given by $\lambda_b dt + o(dt)$ where

$$\lim_{dt \to 0} o(dt)/(dt) = 0$$

Similarly, $\lambda_a dt + o(dt)$ represents the probability that $E_2^n \to E_1^n$ occurs in dt at t, given E_2^n at time t. The parameters $k_{1,i}$ and $k_{2,i}$ represent ordinary rate constants for the addition of monomer to polymer chains in states $\{1\}$ and $\{2\}$, respectively, to form isotactic placements; $k_{1,s}$ and $k_{2,s}$ represent the corresponding rate constants for the addition to form syndiotactic placements. For example, the probability that a given polymer molecule, known to be in the state E_1^n at time t, makes the transition $E_1^n \to E_1^{n+1}$ in dt at t and that this transition results in an isotactic placement is $[M]k_{1,i}\, dt + o(dt)$, where $[M]$ denotes the monomer concentration in molecules per unit volume.

The numbers λ_a, λ_b, $k_{1,i}$, $k_{1,s}$, $k_{2,i}$, $k_{2,s}$ will depend on the temperature and solvent used; we assume here that they are independent of the degree of polymerization n. We also assume that the reactions $\{1\} \rightleftharpoons \{2\}$ are in equilibrium when the monomer is added at $t = 0$ and that $[M]$ does not change appreciably as the polymerization proceeds for $t > 0$. It then

follows[4] that the probability ψ that a polymer molecule selected at random is in the state $\{1\}$ at a given moment t is given by

$$\psi = \frac{\lambda_a}{\lambda_a + \lambda_b} \tag{2}$$

and is independent of t.

The numbers k_1 and k_2, defined by

$$k_1 = k_{1,t} + k_{1,s} \tag{3a}$$

$$k_2 = k_{2,t} + k_{2,s} \tag{3b}$$

are the rate constants for addition of monomer to polymer molecules in the states $\{1\}$ and $\{2\}$, respectively, without regard to tacticity.

3. Diastereosequences

Let ϕ_x ($x = 1,2$) be the probability that a monomer unit, known to have been added to its chain before time t but otherwise selected at random, was added while its chain was in the state $\{x\}$. It is easy to show that ϕ_x is independent of t and is given by[4]

$$\begin{aligned} \phi_1 &= \frac{k_1\lambda_a}{k_1\lambda_a + k_2\lambda_b} \\ \phi_2 &= \frac{k_2\lambda_b}{k_1\lambda_a + k_2\lambda_b} \end{aligned} \tag{4}$$

The quantity α_x defined by

$$\alpha_x = k_{x,t}/k_x \qquad x = 1,2 \tag{5}$$

gives the probability that a placement, known to have been formed in the state $\{x\}$, is isotactic. (In other words, α_x is the probability that a monomer unit is in isotactic placement to its predecessor, given that the unit was added while the polymer molecule was in the state $\{x\}$.)

We denote by $p\{\mathrm{I}\}$ the probability that a placement is isotactic, given no information about the tacticity of other placements or its position along its chain. Clearly

$$p\{\mathrm{I}\} = \phi_1\alpha_1 + \phi_2\alpha_2 \tag{6}$$

Equations (4)–(6) yield

$$p\{\mathrm{I}\} = \frac{\lambda_a k_{1,t} + \lambda_b k_{2,t}}{\lambda_a k_1 + \lambda_b k_2} \tag{7}$$

Letting $p\{\mathrm{S}\}$ be the probability that a placement, selected at random, is syndiotactic, we have

$$p\{\mathrm{I}\} + p\{\mathrm{S}\} = 1 \tag{8}$$

Let $p\{\mathrm{II}\}$ and $p\{\mathrm{SS}\}$ be the probabilities that a randomly selected pair of adjacent placements consists, respectively, of two isotactic placements and two syndiotactic placements. Let $p\{\mathrm{IS_vSI}\}$ be the probability that a pair of adjacent placements is a "heterotactic pair," i.e., either an isotactic placement followed by a syndiotactic placement or a syndiotactic placement followed by an isotactic placement. Note that the diastereosequences here characterized by II, SS, and $\mathrm{IS_vSI}$ are diastereosequences of length two. They each involve two placements or three monomer units. It follows from our definitions that

$$p\{\mathrm{II}\} + p\{\mathrm{SS}\} + p\{\mathrm{IS_vSI}\} = 1 \tag{9}$$

We assume now the mean molecular weight is high enough so that every placement has both a successor and predecessor. Then the following formulae must hold, regardless of the mechanism of polymerization:[3]

$$p\{\mathrm{I}\} = p\{\mathrm{II}\} + {}^1/_2\, p\{\mathrm{IS_vSI}\} \tag{10a}$$

$$p\{\mathrm{I}\} = {}^1/_2\,[1 + p\{\mathrm{II}\} - p\{\mathrm{SS}\}] \tag{10b}$$

$$p\{\mathrm{I}\} = 1 - {}^1/_2 p\{\mathrm{IS_vSI}\} - p\{\mathrm{SS}\} \tag{10c}$$

The equations obtained from these through interchange of the symbols I and S must also hold.

For our present mechanism it can be shown that[4]

$$p\{\mathrm{II}\} = \alpha_1^2\phi_1 + \alpha_2^2\phi_2 - \frac{\lambda_b\phi_1(\alpha_1 - \alpha_2)^2}{k_1\{(\lambda_b/k_1\phi_2) + [\mathrm{M}]\}} \tag{11a}$$

$$p\{\mathrm{SS}\} = (1 - \alpha_1)^2\phi_1 + (1 - \alpha_2)^2\phi_2 - \frac{\lambda_b\phi_1(\alpha_1 - \alpha_2)^2}{k_1\{(\lambda_b/k_1\phi_2) + [\mathrm{M}]\}} \tag{11b}$$

$$ {}^1/_2 p\{\mathrm{SI_vIS}\} = \alpha_1(1 - \alpha_1)\phi_1 + \alpha_2(1 - \alpha_2)\phi_2 + \frac{\lambda_b\phi_1(\alpha_1 - \alpha_2)^2}{k_1\{(\lambda_b/k_1\phi_2) + [\mathrm{M}]\}} \tag{11c}$$

The probabilities considered in eqs. (7)–(11) are, for practical purposes equivalent to concentrations in a large sample. For certain polymers, such as poly(methyl methacrylate), the quantities $p\{\mathrm{I}\}$, $p\{\mathrm{S}\}$, $p\{\mathrm{II}\}$, $p\{\mathrm{SS}\}$, $p\{\mathrm{IS_vSI}\}$ can all be determined by high resolution NMR spectroscopy.[5] Of these five quantities only three can be regarded as independently measured, for the relations (8) and (9) are always used by the experimenter to normalize his data. An example of independently measured data would be any set containing one placement probability (i.e., $p\{\mathrm{I}\}$ or $p\{\mathrm{S}\}$) and two pair probabilities (i.e., any two of the three numbers $p\{\mathrm{II}\}$, $p\{\mathrm{SS}\}$, $p\{\mathrm{IS_vSI}\}$). Each set of independently measured probabilities should obey one of the consistency relations, eqs. (10), which must hold in general, and which serve, not to check a particular mechanism, but rather to convince the experimenter that he has properly identified his spectroscopic

peaks. It is eqs. (7) and (11) which serve to check the applicability of the present mechanism, and we shall discuss their use in Section 5.

General results are known[4] which give for our mechanism the probability of occurrence of diastereosequences of length greater than two. We do not discuss these results here, for the concentrations of diastereosequences of length three or greater (i.e., involving four or more asymmetric chain atoms) are not yet accessible to measurement. The mean length of certain types of diastereosequences are measurable, however.

We define a closed sequence of isotactic placements to be a sequence of $m + 2$ consecutive placements, $m \geq 1$, all of which are isotactic, except for the two at the ends which are both syndiotactic. Let $\mu\{\mathrm{I}\}$ be the mean (number-average) length of the closed sequences of isotactic placements. When the mean molecular weight is high, the following formula should hold for all mechanisms of polymerization:

$$\mu\{\mathrm{I}\} = \frac{p\{\mathrm{I}\}}{p\{\mathrm{S}\} - p\{\mathrm{SS}\}} = \frac{2p\{\mathrm{I}\}}{p\{\mathrm{IS_vSI}\}} \tag{12}$$

We say that a diastereosequence distribution is Bernoullian if formulae of the following type hold: $p\{\mathrm{II}\} = p\{\mathrm{I}\}p\{\mathrm{I}\}$, $p\{\mathrm{IS_vSI}\} = 2p\{\mathrm{I}\}p\{\mathrm{S}\}$, etc. (A more formal definition is given in Section 1 of reference 3.) For a Bernoullian distribution eq. (12) reduces to $\mu\{\mathrm{I}\} = 1/p\{\mathrm{S}\}$. For a general (i.e., non-Bernoullian) diastereosequence distribution, the quantity

$$\rho = \mu\{\mathrm{I}\}p\{\mathrm{S}\} \tag{13}$$

is called the *persistence ratio*, for it gives the ratio of the actual mean length of closed sequences of isotactic placements to the mean length which one would calculate assuming that the distribution be Bernoullian with the same values of $p\{\mathrm{I}\}$ and $p\{\mathrm{S}\}$. It follows from eqs. (12) and (13) that

$$\rho = 2p\{\mathrm{I}\}p\{\mathrm{S}\}/p\{\mathrm{IS_vSI}\} \tag{14}$$

We note that ρ can be calculated from NMR data and gives a convenient measure of "statistical after effects."

For our present mechanism eqs. (7) and (11) yield

$$\rho = \frac{\{(1 - \alpha_1)\phi_1 + (1 - \alpha_2)\phi_2\}(\alpha_1\phi_1 + \alpha_2\phi_2)}{\alpha_1(1 - \alpha_1)\phi_1 + \alpha_2(1 - \alpha_2)\phi_2 + \dfrac{\lambda_b\phi_1(\alpha_1 - \alpha_2)^2}{\{(\lambda_b/k_1\phi_2) + [\mathrm{M}]\}k_1}} \tag{15}$$

4. Molecular Weights

Let $\bar{n}(t)$ and $\bar{n}_w(t)$ be, respectively, the number-average and weight-average degrees of polymerization, and let $r(t)$ be their ratio:

$$r(t) = \bar{n}_w(t)/\bar{n}(t) \tag{16}$$

Assuming that (instantaneous) initiation occurs at $t = 0$, we take as initial conditions

$$\bar{n}(0) = \bar{n}_w(0) = r(0) = 1 \tag{17}$$

A lengthy calculation then yields the following results for our mechanism:[6]

$$\bar{n}(t) = 1 + [\mathrm{M}]\bar{k}t \tag{18}$$

$$\bar{n}_w(t) = 1 + \frac{\{1 + [\mathrm{M}]b/(\bar{k}a)\}([\mathrm{M}]\bar{k}t) - [\mathrm{M}]^2 b(1 - e^{-at})/a^2}{1 + [\mathrm{M}]\bar{k}t} + \bar{k}[\mathrm{M}]t \tag{19}$$

$$r(t) = 1 + \frac{1 + [\mathrm{M}]b/(\bar{k}a)}{\bar{n}(t)} - \frac{1 + [\mathrm{M}]b/(\bar{k}a) + [\mathrm{M}]^2 a^{-2} b(1 - e^{-at})}{\bar{n}(t)^2} \tag{20}$$

where

$$\bar{k} = \psi k_1 + (1 - \psi)k_2 \tag{21a}$$

$$a = \lambda_a + \lambda_b \tag{21b}$$

$$b = 2(k_1 - k_2)^2 \psi(1 - \psi) \tag{21c}$$

The results in eqs. (18)–(20) are mathematically exact and follow from our chemical hypotheses without approximation. It should be emphasized, however, that these results on the molecular weight distribution are far more sensitive than our results on diastereosequence distribution to our idealized assumptions of instantaneous initiation, no irreversible termination, and no chain transfer or depolymerization. For example, a violation of any one of these assumptions renders invalid the following conclusion which follows immediately from eqs. (20) and (18):

$$\text{If } a\bar{k} > 0, \text{ then } \lim_{t \to \infty} r(t) = 1 \tag{22}$$

In reference 6 we give a detailed discussion of the limiting circumstances for which our present molecular weight distribution becomes identical to the Poisson distribution obtained by Flory[7] for the more familiar one-state polymerization.

It should not be concluded from eq. (22) that r is close to 1 for all degrees of polymerization. When $[\mathrm{M}]b \gg \bar{k}a$, our present distribution differs markedly from the Poisson distribution in that eq. (20) yields $r \gg 1$ even for large $\bar{n}$. When $\lambda_a + \lambda_b = 0$, eq. (22) is replaced by the assertion:

$$\text{If } a = 0 \text{ and } \bar{k} \neq 0, \text{ then } \lim_{t \to \infty} r(t) = 1 + \frac{b}{2(\bar{k})^2} \tag{23}$$

This last result can also be derived by considering a mixture of noninteracting one-state polymerizations each yielding a Poisson distribution.

5. Comparison with Experiment

We have discussed earlier[4,6] experimental methods for testing the applicability of the two-state mechanism when certain special restrictive assumptions apply. If all of the six rate coefficients in the reactions (1) are independent of the monomer concentration, a quantitative test is provided by NMR spectroscopy on a series of polymers prepared at different

monomer concentrations but under otherwise identical conditions. According to eqs. (7) and (11), under the present assumptions $p\{\mathrm{I}\}$ should be a constant independent of [M], while $p\{\mathrm{II}\}$ should increase with increasing [M] as

$$p\{\mathrm{II}\} = \delta - \frac{\epsilon}{\gamma + [\mathrm{M}]} \tag{24}$$

where expressions for δ, ϵ, and γ may be obtained by comparison with eq. (11a). Evidence that $p\{\mathrm{I}\}$ is independent of [M] while $p\{\mathrm{II}\}$ varies with [M] in the manner required by eq. (24) would indicate strongly the applicability of the two-state mechanism and would provide a method for determining δ, ϵ, and γ from NMR data.

If it should also happen, under limited conditions at least, for anionic polymerizations carried out in a mixture of a Lewis base and a hydrocarbon, that the rate constants for addition of monomer ($k_{1,t}$, $k_{1,s}$, $k_{2,t}$, and $k_{2,s}$) are independent of the concentration [L] of the Lewis base, but that λ_a and λ_b do depend on [L], it is possible, from NMR data and measurements of the overall rate coefficient $\bar{k}$ of eq. (18) to determine all of the six rate coefficients in reactions (1). It can be shown[4] that

$$\delta = p\{\mathrm{I}\}(\alpha_1 + \alpha_2) - \alpha_1\alpha_2 \tag{25}$$

$$\phi_1 = (p\{\mathrm{I}\} - \alpha_2)/(\alpha_1 - \alpha_2) \tag{26}$$

$$\lambda_b/k_1 = \gamma\phi_2$$

$$\lambda_a/k_2 = \gamma\phi_1 \tag{27}$$

and

$$\phi_2/\phi_1 = (k_2/\bar{k}\phi_1) - (k_2/k_1) \tag{28}$$

Here the values of δ, $p\{\mathrm{I}\}$, and γ, which will vary within a series of polymers prepared at different [L], can be determined by application of eq. (24) to NMR data on polymers prepared at different values of [M] for each value of [L]. By plotting δ versus $p\{\mathrm{I}\}$ (varying [L]) one should, according to eq. (25), get a straight line whose slope and intercept yield the constants α_1 and α_2. Equation (26) then yields ϕ_1 (and, of course, $\phi_2 = 1 - \phi_1$), as a function of $p\{\mathrm{I}\}$, which is, in turn, now a known function of [L]. According to eq. (27) the product of γ and ϕ_1 (or ϕ_2), then yields λ_a/k_2 (or λ_b/k_1) as a function of [L]. From eq. (28) we see that a plot of ϕ_2/ϕ_1 versus $(\bar{k}\phi_1)^{-1}$ should be linear and should yield k_1 and k_2; and on combining these two numbers with the now known values of α_1, α_2, λ_a/k_1, λ_b/k_2, one computes the constants $k_{1,t}$, $k_{1,s}$, $k_{2,t}$, and $k_{2,s}$, and also λ_a and λ_b as functions of [L]. We consider it to be particularly interesting that, at least in principle, the absolute rates λ_a, λ_b of the reactions $E_1^n \rightleftharpoons E_2^n$ are determinable from NMR and rate of polymerization data alone.

We cannot expect all six rate coefficients to be always independent of monomer concentration, since the monomer may form a complex with the

TABLE I
NMR Data on Poly(methyl Methacrylate) Polymerized Anionically in Hydrocarbon Media

Solvent and reference	Initiator	T, °C.	ρ	$p\{I\}$	$\mu\{I\}$	$\mu\{S\}$	$p\{II\}$	$p\{ISvSI\}$	$p\{SS\}$
Toluene[5]	C_6H_5MgBr	0	—	1.0	∞	0	1.0	0	0
Octane[11]	C_6H_5MgBr	0	—	1.0	∞	0	1.0	0	0
Octane[11]	Butyl MgCl	−60	2.8	0.615	7.2	4.5	0.53	0.17	0.30
Toluene[12]	Butyl Li	−80	2.5	0.835	15	3.0	0.78	0.11	0.11
Toluene[5]	Butyl Li	−62	2.1	0.725	7.6	2.9	0.63	0.19	0.18
Toluene[13]	Butyl Li	0	1.8	0.81	9.6	2.3	0.72	0.173	0.107
Toluene[5]	Butyl Li	25	1.7	0.78	7.8	2.2	0.68	0.20	0.12
Toluene[13]	Butyl Li	−70	1.7	0.77	7.5	2.2	0.67	0.205	0.125
Toluene[14]	Butyl Li	−70	1.6	0.80	8	2.0	0.70	0.20	0.10
Ether[13]	Amyl Na	−70	1.4	0.71	4.7	1.9	0.55	0.30	0.14
Petroleum ether[13]	Amyl Na	−70	1.4	0.70	4.7	2.0	0.55	0.30	0.15
Hexane[13]	Amyl Na	−70	1.4	0.61	3.5	2.2	0.43	0.354	0.215
Toluene[13]	Amyl Na	−70	1.3	0.79	6.3	1.7	0.67	0.24	0.09
Toluene[13]	Amyl Na	0	1.3	0.72	4.6	1.8	0.57	0.31	0.12
Toluene[13]	Octyl K	−70	1.2	0.57	2.8	2.1	0.37	0.40	0.23
Toluene[13]	Octyl K	0	1.2	0.56	2.7	2.1	0.35	0.42	0.23

TABLE II
NMR Data on Poly(methyl Methacrylate) Polymerized Anionically in Lewis Bases

Solvent and reference	Initiator	T, °C.	ρ	$p\{S\}$	$\mu\{I\}$	$\mu\{S\}$	$p\{II\}$	$p\{ISvSI\}$	$p\{SS\}$
Dimethoxyethane[13]	Butyl Li	0	1.6	0.70	2.3	5.3	0.17	0.26	0.57
Dimethoxyethane[13]	Butyl Li	−70	1.3	0.81	1.6	6.7	0.07	0.24	0.69
Pyridine[13]	Butyl Li	0	1.2	0.76	1.5	4.8	0.08	0.32	0.60
Pyridine[13]	Butyl Li	−60	1.15	0.76	1.4	4.6	0.07	0.33	0.59
Tetrahydrofuran[15]	Na Naphthalene	−78	1.2	0.72	1.5	3.8	0.12	0.33	0.55
Dimethoxyethane[13]	Amyl Na	0	1.18	0.79	1.5	5.6	0.06	0.28	0.65
Dimethoxyethane[13]	Amyl Na	−70	1.11	0.85	1.3	7.4	0.04	0.23	0.73
Pyridine[13]	Amyl Na	−60	1.08	0.71	1.5	3.6	0.10	0.39	0.51
Pyridine[13]	Amyl Na	0	0.98	0.65	1.5	2.8	0.12	0.46	0.42
$NH_3(l)$[13]	Amyl Na	−70	1.06	0.72	1.5	3.2	0.09	0.38	0.53
Tetrahydrofuran[16]	K Naphthalene	30	1.06	0.535	2.0	2.3	0.23	0.47	0.30
Dimethoxyethane[13]	Octyl K	0	1.00	0.63	1.6	2.7	0.14	0.46	0.40
Dimethoxyethane[13]	Octyl K	−70	0.95	0.63	1.5	2.5	0.12	0.49	0.39
Pyridine[13]	Octyl K	0	0.92	0.60	1.5	2.3	0.14	0.53	0.33
Pyridine[13]	Octyl K	−60	0.90	0.66	1.4	2.7	0.09	0.49	0.42

TABLE III. Data on Poly(methyl Methacrylate) Polymerized Anionically in Mixtures of Toluene with Lewis Bases

Lewis base initiator, and reference	T, °C.	Base, %	ρ	$p\{I\}$	$\mu\{I\}$	$\mu\{S\}$	$p\{II\}$	$p\{SIvSI\}$	$p\{SS\}$	r
Dimethoxyethane[13] (butyllithium)	−30	0	1.8	0.70	6.1	2.6	0.59	0.28	0.18	
	−30	36	1.8	0.51	3.7	3.6	0.38	0.27	0.35	
	−30	62	1.5	0.40	2.5	3.7	0.24	0.32	0.44	
	−30	98	1.5	0.30	2.1	4.9	0.16	0.29	0.55	
	−30	100	1.5	0.25	2	6	(0.12)	(0.25)	(0.63)	
Dimethoxyethane[5] (butyllithium)	−62	50	1.6	0.495	2.7	2.7	0.31	0.32	0.32	
Pyridine[13] (butyllithium)	−30	0	1.8	0.70	6.1	2.6	0.59	0.23	0.18	
	−30	10	1.1	0.26	1.5	4.4	0.0	0.35	0.56	
	−30	20	1.03	0.22	1.3	4.7	0.05	0.33	0.62	
	−30	30	1.11	0.21	1.4	5.3	0.06	0.30	0.64	
	−30	40	1.15	0.23	1.5	5.0	0.08	0.31	0.61	
	−30	50	1.13	0.23	1.5	5.9	0.08	0.31	0.61	
	−30	100	1.18	0.24	1.45	4.7	0.08	0.33	0.59	
Tetrahydrofuran[17] (9-fluorenyllithium)	−62	0.1	1.9	0.82	11	2.4	0.75	0.15	0.10	12
		1	3.9	0.73	15	5.4	0.68	0.10	0.22	4.6
		1	3.0	0.75	13	4.3	0.69	0.11	0.20	4.0
		2.5	3.3	0.53	7	6.2	0.46	0.15	0.39	3.8
		5	3.3	0.27	8	21	0.24	0.07	0.69	9.8
		5								3.2
		7.5	2.2	0.26	3	9	0.17	0.17	0.66	1.6
		7.5								1.6
		10	2.4	0.12	2.7	20	0.07	0.09	0.83	2.1
		10								3.0
		15	1.7	0.13	2	14	0 07	0.13	0.80	2.4
Dioxane[5] (Butyllithium)	−62	40	1.9	0.675	5.9	2.7	0.56	0.23	0.21	
Ether[17] (9-fluorenyllithium)	−62	5	4	0.90	40	4.4	0.88	0.04	0.07	14.6

TABLE IV
NMR Data on Poly(methyl Methacrylate) Polymerized in Toluene at −30°C. with Butyllithium at Two Different Monomer Concentrations[18]

[M], mole/l.	Conversion, %	ρ	$p\{I\}$	$\mu\{I\}$	$\mu\{S\}$	$p\{II\}$	$p\{ISvSI\}$	$p\{SS\}$
0.125	52	1.84	0.82	10	2.2	0.74	0.16	0.10
0.125	94	2.26	0.87	17	2.6	0.82	0.10	0.08
0.125	100[a]	2.25	0.90	23	2.8	0.86	0.08	0.06
0.500	32	1.4	0.67	4.2	2.1	0.52	0.29	0.19
0.500	34	1.4	0.68	4.3	2.1	0.52	0.31	0.17
0.500	73	1.7	0.81	8.5	2.1	0.72	0.18	0.10
0.500	73[b]	2.0	0.86	14	2.3	0.80	0.12	0.08

[a] Polymerized completely, then the same amount of monomer was added and polymerized completely.

[b] Approximately a quarter of the sample polymerized to 73% conversion, removed by extraction with 4-heptanone.

reactive polymer chain, thereby affecting λ_a, λ_b and possibly other rate coefficients as well. In fact, 1:1 complexes of methyl methacrylate with metal salts have been isolated and identified.[8] The observed[9] complicated dependence on [M] of the rate of polymerization of methyl methacrylate with fluorenyl-Li in toluene–tetrahydrofuran mixtures and the finding[10] that polymerizations in toluene at 30°C. initiated by metallic sodium yield highly crystalline polystyrene or poly(methyl methacrylate) only in the range of dilute monomer concentration are evidence for the strong influence of the monomer concentration on the character of the anionic polymerization. The present mechanism can be made compatible with these observations by postulating that the monomer at high [M] complexes with, and alters the concentration of, that reactive state which produces highly isotactic polymer. Thus, only in very special circumstances should we expect the assumption of nondependence of rate coefficients on [M] to be approximately valid. The search for such circumstances is an important goal, however, since they would render possible a quantitative demonstration of the mechanism's applicability.

In Tables I–V we have compiled the NMR data known to us on poly(methyl methacrylate) and poly-α-methylstyrene prepared by ionic polymerizations. These data illustrate the effect of varying the monomer, the initiator, the solvent medium, and the polymerization temperature. Although the results do not provide a definitive test of the mechanism's applicability, we can speculate on their significance using the framework of the two-state mechanism.

The data of Wiles and Bywater[18] on the products of the polymerization of methyl methacrylate in toluene, at −30°C. with butyllithium (Table IV), show a decrease in both ρ and $p\{I\}$ with an increase in the initial [M], and an increase in ρ and $p\{I\}$ as the monomer is consumed in the polymerization. Here, as the evidence cited above suggested, unfortunately the

TABLE V. NMR Data on Poly-α-methylstyrene[18]

Catalyst	Solvent	T, °C.	$p\{S\}$	p	$\mu\{S\}$	$\mu\{I\}$	$\mu\{SS\}$	$p\{ISvSI\}$	$p\{II\}$
BF_3	Toluene	−78	0.95	0.9	17	0.9	0.89	0.11	—
$AlCl_3$	Toluene	−78	0.925	1	12	1	0.85	0.15	—
$SnCl_4$	Toluene	−78	0.925	1	12	1	0.85	0.15	—
$SnCl_4$	Nitromethane	−30	0.91	0.9	10	1	0.82	0.18	—
$TiCl_4$	Toluene	−78	0.91	0.9	9.6	1	0.81	0.14	—
$SnCl_4$	Ethylene chloride	−35	0.87	0.9	6.7	1	0.74	0.26	—
Butyl Li	Cyclohexane	4	0.85	0.8	5.5	1	0.69	0.31	—
$AlEt_3/TiCl_4$	Benzene	25	0.80	0.9	4.6	1.1	0.62	0.35	0.03
x-ray		30	0.79	1	5	1.3	0.63	0.32	0.05
AIBN at 600 atm (free radical)		100	0.75	1	3.8	1.3	0.55	0.40	0.06
Na	Tetrahydrofuran	0	0.67	1	1.5	3	0.44	0.45	0.11
Na-Naphthenide	Tetrahydrofuran	−78	0.63	1	1.5	2.6	0.39	0.48	0.13

monomer participates in the reactions which control the nature and concentration of the reactive states, and we cannot assume that all of the rate constants are independent of [M].

In the anionic polymerization of methyl methacrylate in hydrocarbons (Table I), predominantly isotactic polymers are formed with values of ρ and $p\{I\}$ decreasing in the order $Li^+ > Na^+ > K^+$, i.e., decreasing on going from strongly to weakly complexing cations.[8,13] Predominantly syndiotactic polymers are formed in polymerizations in Lewis bases (Table II), with ρ, and now not $p\{I\}$, but rather $p\{S\}$, decreasing in the order $Li^+ > Na^+ > K^+$;[13,16] the parameters here are also sensitive to the temperature and to the nature of the Lewis base. In mixed solvents (Table III), $p\{I\}$ decreases with increasing [L] in toluene;[9,13,17,20] although ρ may increase with increasing [L] at low [L], it invariably decreases at higher [L].

It appears that in the polymerization of methyl methacrylate the use of a strongly complexing cation tends to yield values of ρ appreciably greater than one. The scanty available data on molecular weights indicates that conditions which produce large ρ also produce large r. Under the two-state mechanism, assuming of course that $\alpha_1 \neq \alpha_2$, $k_1 \neq k_2$, we interpret this as meaning that the reactions $\{1\} \rightleftharpoons \{2\}$ are slow relative to the addition reactions, (1c–1f). Glusker and Galluccio[17] found that they could separate the product of polymerization of methylmethacrylate by fluorenyl-Li in a toluene–tetrahydrofuran mixture into high molecular weight fractions which were highly isotactic and lower molecular weight fractions which were less isotactic; Wiles and Bywater[18] have extracted with 4-heptanone (Table IV) a poly(methyl methacrylate) fraction more isotactic than the whole polymer prepared in toluene with butyllithium. Further, binodal molecular weight distributions in the products of polymerizations of methyl methacrylate in such systems were observed by a number of workers.[3,9,18,20,21] These observations suggest that the reactions $\{I\} \rightleftharpoons \{2\}$ can be very much slower than the addition reactions. The fact that the reported values of r for these polymers are large and do not seem to approach 1 at large $\bar{n}$, even though initiation has been shown to be instantaneous and no irreversible termination occurs, is in accord with this hypothesis.

We are led, therefore, to explore the consequences of the assumption that in the anionic polymerization of methyl methacrylate in the presence of strongly complexing cations we have, as a rough approximation, $a = \lambda_a + \lambda_b = 0$, but $\psi = \lambda_a/(\lambda_a + \lambda_b) \neq 0$ and $1 - \psi \neq 0$. We now assume ψ, and hence ϕ_1 and ϕ_2, to be dependent on [L], but take α_1 and α_2 to be (approximately) independent of [M] and [L]. From eqs. (6) and (11a) we then obtain

$$p\{II\} = (\alpha_1 + \alpha_2)p\{I\} - \alpha_1\alpha_2 \tag{29}$$

It follows that, for each initiator and solvent pair, if one varies [L], plots of $p\{II\}$ versus $p\{I\}$ should yield (approximately) straight lines. Using the data of Table III, we have found this to be the case with values of α_1

approximately equal to 0.9 and of α_2 in the range 0.05–0.15, with the actual values depending on the solvent pair and initiator. If such a representation of data is valid, it is suggested that the polymerizations in the different mixtures are similar in that each case there are two reactive species, changing only very slowly from one to the other: one, $\{1\}$, producing quite isotactic chains (very high values of α_1), and the other, $\{2\}$, producing moderately syndiotactic chains (low values of α_2).

Glusker and co-workers[9] have proposed from kinetic evidence that more than two states are involved in the polymerization of methyl methacrylate by fluorenyllithium in mixtures of toluene with tetrahydofuran or ether. Bywater[22] has come to similar conclusions. In the cases where the reactions $\{x\} \rightleftharpoons \{y\}$ are slow, a multistate mechanism becomes equivalent to a two-state mechanism, as far as NMR spectra are concerned, if the α_x's fall into only two separated sets, one with α_x close to 0 and the other with α_x close to one.

If, in the highly stereospecific anionic polymerization of methyl methacrylate it is really true that λ_a and λ_b are practically zero, then we have the case of two reactive states polymerizing independently, with only rare conversion of one to the other form. Such a polymerization is, in a sense, heterogeneous, and we see that we have here, at best, a limiting case of the dynamic equilibrium between two states which we have treated theoretically. Experimentally, this means that one would have to reduce the monomer concentration by a very large factor in order to obtain a measurable reduction of ρ. It is intriguing to note that if the reactions $\{1\} \rightleftharpoons \{2\}$ are slow, once the species $\{1\}$ and $\{2\}$ are formed, their relative concentrations should change only slowly upon subsequent changes in the medium. Since the nature of the polymerization is sensitive to the polymerization medium, however, it appears that the initial reactions $E_1^n \rightarrow E_2^n$ for, say, $n < 10$ are sensitive to the medium; i.e., it appears that the relative concentrations of $\{1\}$ and $\{2\}$ are affected by events occurring early in the polymerization, but become "frozen" at fixed values when n is large. This picture requires that we modify our original mathematical assumption that the rate coefficients λ_a and λ_b be independent of n. This picture is in accord with the conclusion of Glusker and co-workers[9] that the kinetics of anionic polymerizations of methyl methacrylate are strongly affected by events occurring during the first few seconds of the reaction, and by their observation that the rate of polymerization depends in a complicated way on the initial monomer concentration but decreases simply in proportion to [M] as the monomer is converted to polymer during the polymerization. On the other hand, the observation of Wiles and Bywater[18] that ρ and $p\{I\}$ increase as the monomer is consumed in the polymerization of methyl methacrylate in toluene with butyllithium (Table IV) suggests that here, even when n is large, $\lambda_a + \lambda_b$ is not negligible, and may be affected by [M].

In the anionic polymerization of methyl methacrylate in the presence of less strongly complexing cations, e.g. K^+, values of ρ of 1, or only slightly greater than 1, are observed. Evidently here either $\alpha_1 \cong \alpha_2$, or the approx-

imation $\lambda_a + \lambda_b = 0$ is not even roughly applicable, or both. Systematic studies of the dependence of the NMR spectrum and of the molecular weight distribution on the monomer concentration and other variables in the polymerization of methyl methacrylate with less strongly complexing cations are now being started in this laboratory.

The NMR data on poly-α-methylstyrene prepared in ionic polymerizations[19] (Table V) correspond to Bernoulli trial statistics ($\rho = 1$). It is known that polymers of narrow molecular weight distribution ($r < 1.05$) are obtainable in the anionic polymerization of α-methylstyrene and of styrene as well. If the two-state mechanism is applicable for these monomers, it appears that for them the rates of the reactions $\{1\} \rightleftharpoons \{2\}$ are much greater than the rates of the addition reactions. Actually, the precise kinetic studies of Bywater and Worsfold[23] on the polymerization of styrene initiated by butyllithium in mixtures of toluene with tetrahydrofuran indicate that at least three reactive states participate in the polymerization and that the equilibrium between the various states is very rapid indeed. It follows that in attempts to demonstrate the two-state mechanism for these monomers one would have to increase [M] many fold to obtain a measurable increase in ρ.

We are grateful to Dr. D. L. Glusker of the Rohm and Haas Company for helpful suggestions.

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Synopsis

The two-state mechanism was proposed to explain the stereoblock structures which occasionally result from homogeneous anionic polymerizations. This mechanism postulates that a growing polymer chain has two reactive states, $\{1\}$ and $\{2\}$, in dynamic equilibrium, both capable of adding monomer, but each with its own rate and stereospecificity. Here we gather together those implications of the mechanism, for the diastereosequence and molecular weight distributions, which appear to be accessible to experimental verification, and we use them to interpret existing data on homogeneous anionic polymerizations with particular emphasis on the polymerization of methyl methacrylate.

Résumé

On propose un mécanisme en deux étapes pour expliquer les structures "stéréobloc," qui parfois résultent des polymérisations anioniques en milieu homogène. Le mécanisme admet que la chaîne polymérique croissante a deux états de réactivité $\{1\}$ et $\{2\}$ en équilibre dynamique. Tous les deux sont capables d'additionner le monomère mais avec une vitesse et une stéréospécificité différente. Nous rassemblons ici les conséquences de ce mécanisme tant pour la diastéré séquence que pour la distribution du poids moléculaire, qui semblent accessibles à la vérification expérimentale. Nous employons les dites conséquences pour interprêtér les résultats qui existent pour les polymérisations anioniques en milieu homogène et spécialement dans le cas de la polymérisation du méthacrylate de méthyle.

Zusammenfassung

Zur Erklärung der "Stereoblock"-Struktur, die gelegentlich bei homogener anionischer Polymerisation auftritt wurde ein "Zwei-Zustands-Mechanismus" vorgeschlagen. Bei diesem Mechanismus wird angenommen, dass eine wachsende Polymerkette in zwei Zuständen, $\{1\}$ und $\{2\}$, auftreten kann, die miteinander im dynamischen Gleichgewicht stehen und beide Monomeres addieren können, aber jeder mit einer verschiedenen Geschwindigkeit und Stereospezifität. Hier werden diejenigen Folgerungen aus diesem Mechanismus auf die Diastereosequenz- und Molekulargewichtsverteilung behandelt, die einer experimentellen Überprüfung zugänglich sind. Sie werden zu einer Interpretation vorhandener Daten bezüglich der homogenen anionischen Polymerisation mit besonderer Berücksichtigung der Polymerisation von Methylmethacrylat herangezogen.

Discussion

P. H. Van Der Meij (*Hollande*): Recently several investigators have prepared polymethyl methacrylates which are characterized (in your notation) by a $p < 1$ (down to $p = 0{,}8$). Can your theory be applied to explain this phenomenon?

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Stereospecific Polymerization of Vinyl Monomers by Ionic Mechanism in Homogeneous Systems

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1. INTRODUCTION

The stereospecific polymerization of vinyl ether has been studied by our research group.[1-10] In the case of homogeneous catalyst, it was found that (*1*) the stereospecific polymerization could proceed in the homogeneous systems, (*2*) the isotactic polymer was obtained in a nonpolar solvent at low temperature, and (*3*) the kind of counterion affected the stereospecificity of polymers.[1-8] On the other hand, with heterogeneous catalysts, isotactic polyvinyl alkyl ethers were produced even at a relatively high temperature.[9,10]

The reaction mechanism was discussed in these reports, but the interaction between a counterion and a substituent of monomer was not considered. The purpose of this paper is to describe the effect of various conditions on the stereospecific polymerization of vinyl ethers and other vinyl monomers, and to clarify the interaction between a counterion and a substituent of monomer.

2. EFFECT OF TEMPERATURE ON THE STEREOREGULARITY OF POLYMERS

2.1. Cases of Large Effect of Polymerization Temperature

a. Polymerization of Styrene Catalyzed by n-Butyllithium (BuLi)

The polymerization was studied at temperatures from -45 to $+30$°C. under N_2 atmosphere by the usual method. The stereoregularity of polystyrene was estimated from infrared spectral data. Infrared spectra clearly indicated stereoregularity of polystyrene by the absorption bands at 1364, 1070, and 983 cm.$^{-1}$, as shown in Figure 1.[11,12] We used the ratio S_a (D_{1157}/D_{1070}) as a measure of the stereoregularity, because this value did not change on heating, unlike the values of D_{1157}/D_{1364} and D_{1157}/D_{983}. It seems that the absorption at 1070 cm.$^{-1}$ is due to a stereoregularity at the monomer level (i.e., not in long sequences), for its intensity did not change on crystallization.

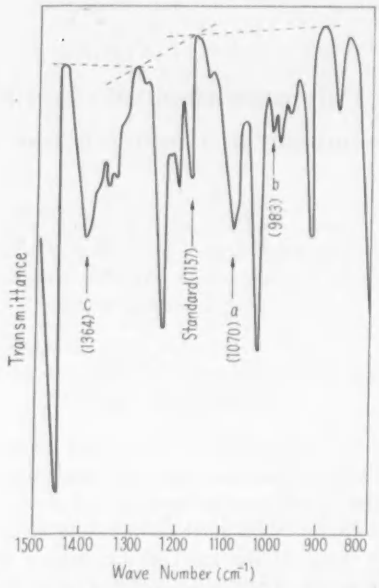

Fig. 1. Infrared spectrum of isotactic polystyrene obtained with BuLi catalyst at −45°C.

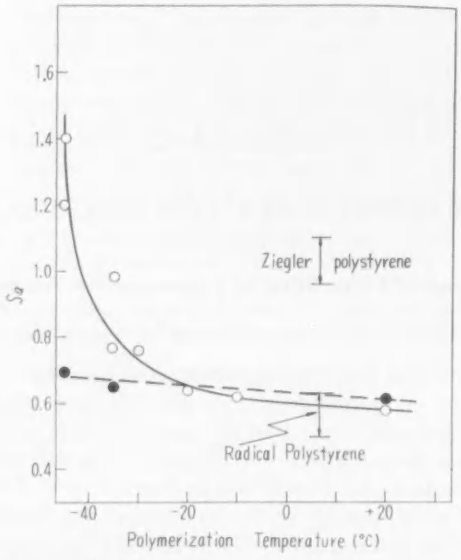

Fig. 2. Effect of polymerization temperature on the stereoregularity of polystyrene obtained: (○) in toluene; (●) in THF. [Styrene] = 1.92 mole/l.; [BuLi] = 10^{-2} mole/l.

Figure 2 shows the effect of polymerization temperature on S_a of polystyrene. The results shown in Figure 2 indicate that S_a was the same as that for a radical polystyrene when styrene was polymerized at −20°C. or above in toluene by BuLi, but with polymerization at −30°C. or below, the S_a value increased markedly. The polymer obtained at low temperature showed almost the same infrared spectra as Ziegler polystyrene; and also its solubility in various solvents was the same as that of Ziegler polystyrene. When tetrahydrofuran (THF) was used as a solvent, however, the stereoregularity of the resultant polymer was almost constant (atactic) in this range of temperature.

b. Polymerization of Vinyl Ethers Catalysed by $BF_3 \cdot OEt_2$

It is well known that isotactic polyvinyl ether is obtained by homogeneous cationic catalysts when the polymerization is carried out in a nonpolar solvent at low temperature. The effect of temperature on the stereoregularity of polyvinyl isobutyl ether (PVIBE) is illustrated in Figure 3. In the Figure 3, the ratio D_{988}/D_{970} was used to determine the relative degree of the stereoregularity. This relation between infrared spectra and the stereoregularity was reported by Iwasaki.[13] In all our experiments the highest value of D_{988}/D_{970} was 1.00 and the lowest was in the range 0.1–0.05. Figure 3 shows that in nonpolar solvents the stereoregularity of

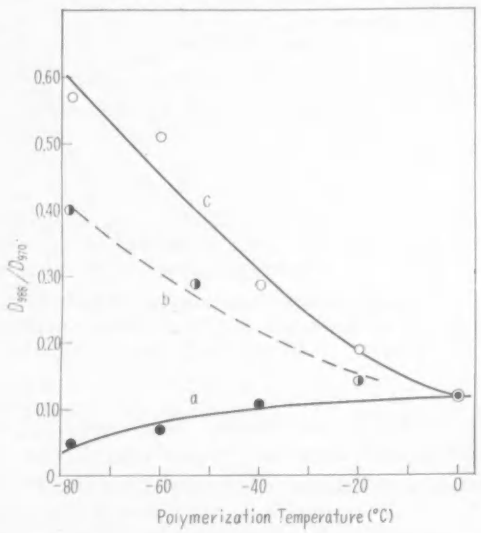

Fig. 3. Effect of polymerization temperature on the stereoregularity of polyvinyl isobutyl ether in homogeneous polymerization: (*a*) [VIBE] = 4 vol.-%, [$BF_3 \cdot OEt_2$] = 4–25 mmole/l., solvent nitroethane; (*b*) [VIBE] = 2 vol.-%, [$Al(C_2H_5)Cl_2$] = 18 mmole/l., solvent *n*-hexane; (*c*) [VIBE] = 4 vol.-%, [$BF_3 \cdot OEt_2$] = 4–24 mmole/l., solvent toluene.

PVIBE greatly decreased with increasing of polymerization temperature in the homogeneous polymerization, and a more regular polymer was produced by $BF_3 \cdot OEt_2$ than be $AlEtCl_2$.

In nitroethane, on the other hand, an atactic polymer was obtained over this range of temperature.

2.2. Cases of Small Effect of Polymerization Temperature

a. Polymerization of Methyl Methacrylate (MMA) Catalyzed by BuLi

MMA was polymerized by BuLi. The polymerization of MMA by anionic catalysts has been extensively studied by Kern et al.,[14] and so we will

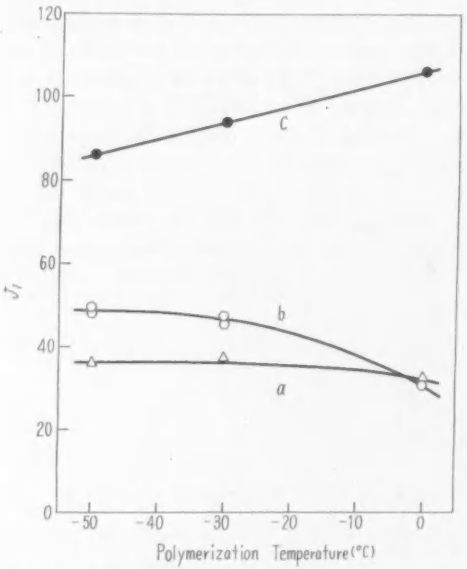

Fig. 4. Effect of polymerization temperature on the stereoregularity of PMMA obtained with BuLi catalyst in the homogeneous polymerization: (*a*) [MMA] = 3 vol.-%, solvent toluene; (*b*) [MMA] = 10 vol.-%, solvent toluene; (*c*) [MMA] = 10 vol.-%, solvent THF.

merely describe briefly our own results. Now, putting $J_1 = 179\ (D_{9\cdot3}/D_{10\cdot1}) + 27$ according to Goode et al.,[15] we can relate J_1 and polymerization temperature as shown in Figure 4. The smaller the J_1 value, the higher the isotacticity is found. J_1 as well as S_a was almost unchanged on heating.* In this system, the isotacticity of resultant polymers did not decrease as the temperature was raised in the range from -50 to $0°C$.

* Goode selected the J value as a measure of the stereoregularity, where $J = (J_1 + J_2)/2$ and $J_2 = 81.4\ (D_{5\cdot75}/D_{7\cdot20}) - 43$. As J_2 is changed by crystallization, we chose to use the J_1 value in this paper.

b. Polymerization of Vinyl Ethers Catalyzed by the Metal Sulfate–Sulfuric Acid Complex

VIBE was polymerized by metal sulfate–sulfuric acid (MS) complexes at various temperatures. Although these complexes were heterogeneous catalysts,[9,10] this study was performed because its result gave an important fact for the homogeneous polymerization as shown below.

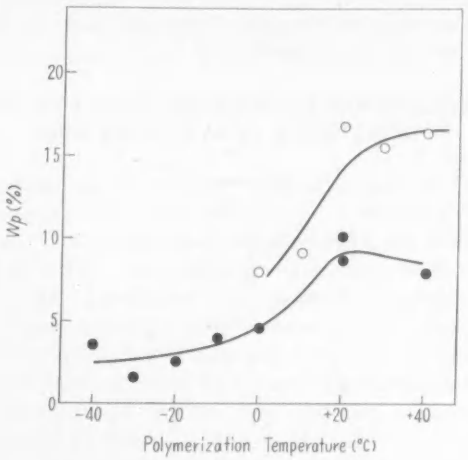

Fig. 5. Effect of polymerization temperature on the stereoregularity of polyvinyl isobutyl ether in heterogeneous polymerization: (○) slow mechanical stirring; (●) vigorous magnetic stirring. [VIBE] = 30 vol.-%, [*n*-hexane] = 70 vol.-%; [$Al_2(SO_4)_3$–H_2SO_4 complex] = 0.7 g./l.

Stereoregular PVIBE was obtained at high temperature as shown in Figure 5 with the use of MS complexes. In these experiments, W_p (the weight per cent of the highly stereoregular portion which was insoluble in 0.5 g./100 ml methyl ethyl ketone solution at 30°C.) was used as a measurement of relative stereoregularity.[10] This insoluble portion had an excellent

TABLE I
Effect of Polymerization Temperature on the Stereoregularity of Polymers

Monomer–catalyst system	Stereoregularity	
	High temperature	Low temperature
Vinyl ether–$BF_3 \cdot OEt_2$	None	Good
Vinyl ether–MS complex	Good	Good
Styrene–BuLi	None	Good
MMA–BuLi	Good	Good
2-Vinylpyridine–R-metal(Natta)	Good	Good
4-Vinylpyridine–R-metal(Natta)	None	—

isotactic structure. Figure 5 shows that the stereoregularity of polymer increased slightly as temperature was raised; also, the decrease of stereoregularity when the polymerization was carried out with vigorous stirring suggested the necessity of a catalyst surface for the stereospecific polymerization in such a system.

From these results, it was found that, with the same catalyst, the temperature dependence varied with the kind of monomers; also a similar relation was observed for any one monomer in polymerization with different catalysts. These relations are summarized in Table I; Natta's results for vinylpyridines[16] are also included there.

3. COORDINATION POLYMERIZATION AND SIMPLE COUNTERION POLYMERIZATION

Two cases of stereospecific polymerization in the homogeneous ionic systems may be considered. One is the case in which the stereoregularity is greatly affected by polymerization temperature and the stereoregular polymer is obtained only at low temperature. (This case is generally recognized as homogeneous cationic polymerization.) The other is the case in which the stereoregularity is not affected by polymerization temperature and the stereoregular polymer is produced at high temperature.

Natta[17] has indicated that when the monomer contains two groups which can coordinate to a catalyst, both anionic and cationic stereospecific polymerizations may take place with a soluble catalyst. However, it may be impossible to consider that the substituent of a monomer and the counterion of catalyst can always form complexes. It seems especially, improbable that a counter-anion should form a complex with the ether oxygen of vinyl ether.

So we propose to divide the homogeneous stereospecific polymerization into the following two groups.

The first group has little or no tendency toward complex formation between the counterion and the monomer substituent, and the stereoregularity is controlled mainly by the steric hindrance of substituents and the interaction between a growing chain end and a counterion. The styrene–BuLi and vinyl ethers–$BF_3 \cdot OEt_2$ systems are in this case.

In the second group there is a strong interaction between the counterion and the substituent of monomer, and this case corresponds to the so-called coordinate polymerization. MMA–BuLi, vinyl ethers–MS complex, and vinyl-pyridines–anionic catalysts systems are in this case.

It appears that in the first group the repulsion energy between substituents may be about 1–2 kcal./mole,[18] but in the second group the energy of complex formation is much larger. Therefore, the difference between the energies of these interactions perhaps causes the difference in temperature dependence.

It is not clear why the complex formation between a counterion and a substituent of a monomer produces a polymer of higher stereoregularity

(it may not be known whether the substituent concerned in the complex formation is the attacking monomer or the growing chain end).

4. IMPORTANCE OF COUNTERION AND HOMOGENEITY FOR ISOTACTIC POLYMERIZATION

When the counterion is not involved and the stereoregularity of a polymer is controlled only by the steric effect between substituents of monomer, the mechanism of the stereospecific polymerization is the same as that of the radical polymerization, and a syndiotactic polymer may be obtained.

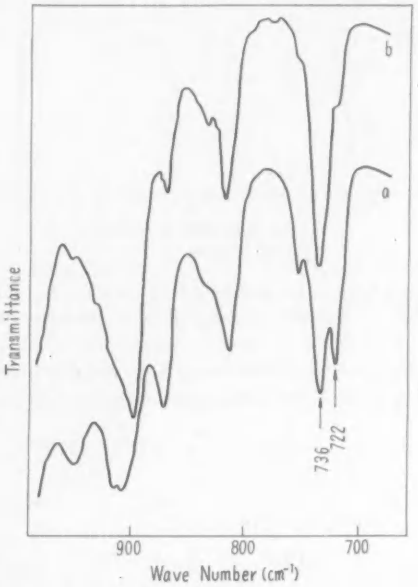

Fig. 6. Infrared spectra of PVtBE: (*a*) syndiotactic polymer, nitroethane solvent; (*b*) isotactic polymer, toluene solvent. $[M_0]$ = 0.376 mole/l.; $[BF_3 \cdot OEt_2]$ = 5.1 mmole/l.; polymerization temperature −78°C.

Formation of syndiotactic polymer was reported in the case of an anionic polymerization of MMA in polar solvents. But in the first group described in Section 3 above, syndiotactic polymer is not produced. When vinyl *tert*-butyl ether (VtBE) was polymerized in a polar solvent ($C_2H_5NO_2$) in the presence of $BF_3 \cdot OEt_2$ at low temperature, polyvinyl *tert*-butyl ether (PVtBE) containing a syndiotactic part was obtained. The infrared spectra ratio (D_{722}/D_{736}) was used as a measure of stereoregularity (Fig. 6), and the isotactic PVtBE has a small value of D_{722}/D_{736}. The relation between the solvent composition and D_{722}/D_{736} of resultant polymers is shown in Figure 7.

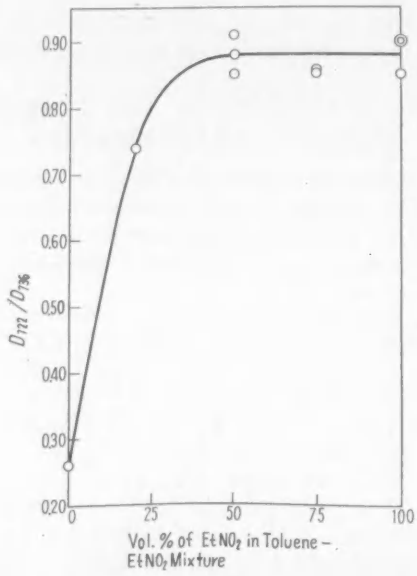

Fig. 7. Effect of polar solvent on the stereoregularity of PVtBE. $[M_0] = 0.376$ mole/l, $[BF_3 \cdot OEt_2] = 5.1$ mmole/l.; polymerization temperature $-78°C$.

On the other hand, polyvinyl alcohol (PVA) was obtained by the cleavage of the ether bond of PVtBE by HBr as shown in eq. (1):[8]

$$\text{—(CH}_2\text{—CH)—}_n \xrightarrow{\text{HBr}} \text{—(CH}_2\text{—CH)—}_n \quad (1)$$

(O—C(CH$_3$)$_2$—CH$_3$ on the left; OH on the right)

It was already previously reported[19] that an absorption at 916 cm.$^{-1}$ in PVA showed a syndiotactic structure. The relation between D_{722}/D_{736} of PVtBE and D_{916}/D_{849} of PVA is shown in Figure 8. Infrared spectra of PVA were measured by KBr disk method without any heat-treatment of polymers and those of PVtBE were measured on polymer films. In such a procedure, D_{916}/D_{849} of PVA obtained from radical-initiated PVAc (polymerization temperature $+60°C$.) was 0.26–0.28, and that of radical-induced polyvinyl trifluoroacetate (polymerization temperature $+60°C$.) was 0.36–0.38. These values slightly decreased on heating.

It is clear from Figures 7 and 8 that syndiotactic polymers are produced in a polar solvent. This result shows that the counterion is necessary to produce an isotactic polymer.

There was no certain evidence that the truly homogeneous system was more profitable for the stereospecific polymerization than the heterogeneous

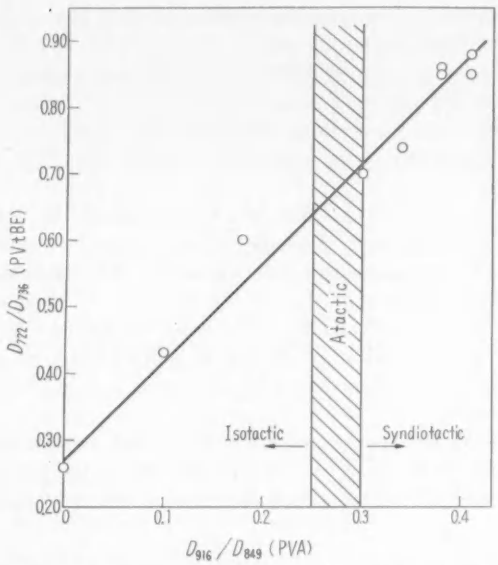

Fig. 8. Relation between D_{722}/D_{736} of PVtBE and D_{916}/D_{849} of PVA.

one. We already reported that in the polymerization of VIBE catalyzed by $BF_3 \cdot OEt_2$ at $-78°C.$, the polyvinyl ethers obtained from the homogeneous polymerization system had a more isotactic structure than those obtained from a related heterogeneous system.[2] The homogeneous polymer-

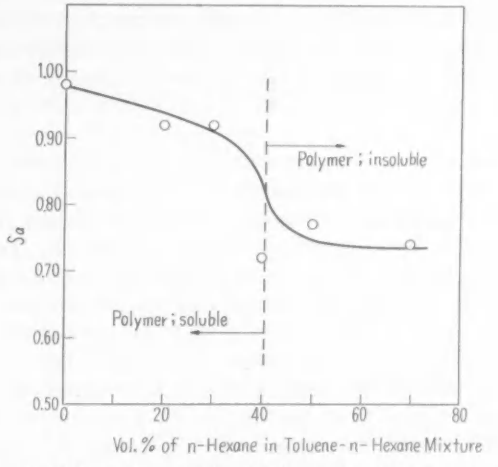

Fig. 9. Effect of addition of a nonsolvent (*n*-hexane) on the stereoregularity of polystyrene. [Styrene] = 1.92 mole/l.; [BuLi] = 10 mmole/l.; polymerization temperature $-30°C.$

ization was carried out by addition of monomer in a solvent–catalyst solution, while the heterogeneous polymerization (the so-called polyphase polymerization or proliferous polymerization),[20] was carried out by addition of catalyst in a monomer–solvent solution. In the homogeneous polymerization, the reacting system was apparently homogeneous, and the appearance of polymerization was quite different from that in the heterogeneous case.

We therefore examined the effect of a nonsolvent on the stereospecificity of polystyrene in the homogeneous polymerization of styrene by BuLi using a mixed solvent of toluene and *n*-hexane. When *n*-hexane increased and the solution began to be cloudy, the isotacticity of polymer suddenly decreased, as shown in Figure 9. This result supported the fact that the stereospecific polymerization of styrene as well as VIBE proceeded easily in the homogeneous system where an attacking monomer and a polymer could freely move.

From these results, it was found that the existence of a counterion was necessary for preparation of the isotactic polymer in the homogeneous system and the yield of this reaction was increased by the homogeneity of the system.

5. IMPORTANCE OF COMPLEX FORMATION IN STEREOSPECIFIC POLYMERIZATION AT HIGH TEMPERATURE

5.1. Effect of Additives

In the polymerization of MMA with BuLi, the addition of ether, which has a large tendency for complex formation with $Li^{\oplus}$, decreased the stereoregularity of PMMA.[14] As already reported,[4] an addition of methanol to be VIBE–$BF_3 \cdot OEt_2$ system did not markedly change the isotacticity of PVIBE. This fact suggested that the complex between a counteranion and an electron donor, e.g., methanol, was not stronger than that of $Li^{\oplus}$ and ether.

On the other hand, in the polymerization with the heterogeneous catalyst which formed a complex between a counterion and a substituent of a monomer, an addition of methanol or ether remarkably decreased the stereoregularity of the polymers, as shown in Table II. To confirm the result of Table III, the effect of a small amount of ether was examined (Table III). In this experiment, the reaction system was divided into two parts; an upper part (a clear solution which did not contain catalyst particles) and a lower part (a medium which surrounded catalyst particles).[10] When ether was directly added to a catalyst before addition of monomer, the isotacticity of polymer which was produced in the lower part of the reaction system decreased.

These results show that an electron donor was added to a positive part of a catalyst (this part may interact with a substituent of a monomer), and this interaction interfered with complex formation between monomer and

TABLE II
Effect of an Addition of Electron Donors on the Stereoregularity of PVIBE in Heterogeneous Systems[a]

Catalyst washing[b]	Polymerization time, min.	Conversion %	[η]	D_{990}/D_{970}	Highly stereoregular portion, %[c]
None	24	92.7	1.01	0.21	8.6
$(C_2H_5)_2O$	24	80.4	0.95	0.17	1.0
CH_3OH	27	89.4	0.45	0.15	2.6

[a] [VIBE] = 30 vol-%, *n*-hexane = 70 vol.-%, temperature = +20°C, [$Al_2(SO_4)_3$–H_2SO_4 complex] = 0.3 g./l.

[b] Catalyst (10 mg.) was washed with diethyl ether (1 ml.) or methanol (0.5 ml.) at room temperature before the polymerization procedure.

[c] Insoluble part in methyl ethyl ketone at 30°C.

TABLE III
The Effect of Small Amount of Ether on the Stereoregularity of PVIBE[a]

$(C_2H_5)_2O$ addition, mmole/l.	Part	Conversion, %	D_{988}/D_{970}	W_p, %
None	Upper	12	0.24	5
	Lower	25	0.43	28
20 (added after monomer)	Upper	16	0.09	8
	Lower	28	0.48	28
20 (added before monomer)	Upper	16	0.29	12
	Lower	23	0.34	21

[a] [VIBE] = 10 vol.-%; [*n*-hexane] = 90 vol.-%; [$Al_2(SO_4)_3$–H_2SO_4 complex] = 0.5 g./l.; time 100 min.; Temperature +30°C.; $[(C_2H_5)_2O]/[Al] = 10$.

catalyst. It is interesting that the effect of additives is different in the cationic polymerization of the same vinyl ether.

5.2. Effect of Bulkiness of Substituent

If the main reason for the heterogeneous stereospecific polymerization of vinyl alkyl ethers is the complex formation between a counterion and an ether oxygen atom of the monomer, it may be supposed that a monomer having a bulky substituent does not produce a stereoregular polymer in the this type of polymerization. To clarify this point we polymerized vinyl methyl, vinyl isobutyl, and vinyl *tert*-butyl ethers with MS-complex catalyst. As shown in Figure 10, isotactic polymers were obtained from vinyl methyl ether (VME) and VIBE, but we could not obtain the isotactic PVtBE under similar conditions. D_{994}/D_{785} as reported by Iwasaki,[21] was used as the measure of stereoregularity of polyvinyl methyl ether (PVME).

Otherwise, as it is unnecessary to form a complex in the homogeneous stereospecific polymerization with $BF_3 \cdot OEt_2$, it may be expected that the larger the substituent is, the more regular the polymer is. The results of the homogeneous polymerization of VtBE by $BF_3 \cdot OEt_2$ are shown in

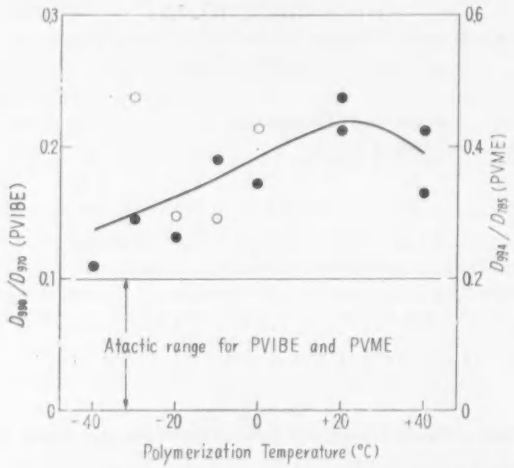

Fig. 10. Effect of polymerization temperature on the stereoregularity of various polyvinyl ethers obtained by heterogeneous catalysis; (○) [VME] = 20 vol.-%, [toluene] = 80 vol.-%, [$Al_2(SO_4)_3$–H_2SO_4 complex] = 1.0 g./l.; (●) [VIBE] + 30 vol.-%, [*n*-hexane] = 70 vol.-%, [$Al_2(SO_4)_3$–H_2SO_4 complex] = 0.5 g./l.

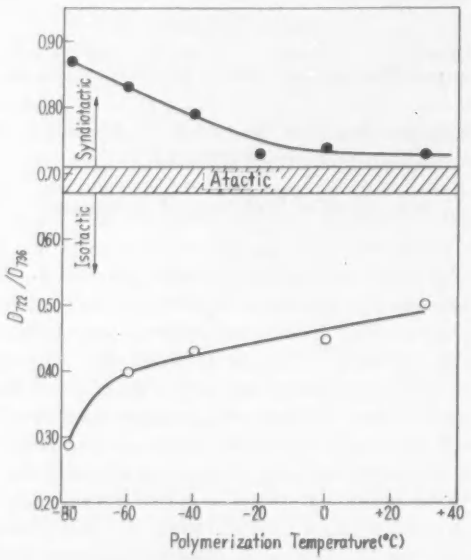

Fig. 11. Effect of polymerization temperature on the stereoregularity of PVtBE obtained in homogeneous polymerization: (○) toluene; (●) nitroethane. [VtBE] = 4 vol.-%; [$BF_3 \cdot OEt_2$] = 4–7 mmole/l.

Figure 11. Figure 11 shows that there was a difference between the structure of polymers obtained in a nonpolar solvent and that in a polar solvent at +30°C. As shown in Figure 3, no difference of the stereoregularity was recognized between a polymer obtained in a nonpolar solvent and that in a polar solvent, even at 0°C. These results suggest that the bulkiness of a substituent of a monomer plays a more important role than that of the interaction between a substituent and a counterion for determining the stereoregularity of polymers in homogeneous polymerization.

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Synopsis

From the dependence of the stereoregularity of vinyl polymers on polymerization temperature, it is estimated that there are two cases of stereospecific polymerization; in the first group there is little or no tendency toward a complex formation between a counterion and the monomer substituent; in the second group there is a strong interaction between the monomer and catalyst. In the first group, a stereoregular polymer is obtained only at low temperature, but a highly regular polymer is produced at high temperature in the latter. The existence of a counterion is necessary to prepare the isotactic polymer in the homogeneous system, and the yield of isotactic polymerization becomes greater with increasing homogeneity of the system. Results of the polymerization of vinyl ethers, styrene, and methyl methacrylate indicate that this classification may be reasonable, but it is not clear at present why the stereoregular polymer is pro-

duced under the conditions of complex formation between a counterion and the monomer substituent of a monomer.

Résumé

L'effet de la température de polymérisation sur la stéréorégularité de polymères vinyliques suggère qu'il existe deux cas de polymérisation stéréospécifique. Dans le premier il n'y a presque pas de tendance à la formation de complexes entre le contre-ion et un substituant du monomère et dans le deuxième cas il existe de fortes interactions entre le monomère et le catalyseur. Un polymère stéréorégulier ne peut être formé dans le premier groupe qu'à basse température, tandis que dans l'autre groupe un polymère très régulier est formé à haute température. La présence d'un contre-ion est indispensable pour préparer du polymère isotactique en système homogène. Par l'homogénéité du système, la polymérisation isotactique devient plus profitable. La polymérisation des éthers vinyliques, du styrène et du méthacrylate de méthyle est un argument en faveur de cette classification. Just' uà présent on ne sait pas très bien pourquoi un polymère stéréospécifique est formé sous l'influence d'un contre-ion, formant un complexe avec un substituant du monomére.

Zusammenfassung

Aus der Abhängigkeit der Stereoregularität von Vinylpolymeren von der Polymerisationstemperatur ergeben sich zwei verschiedene Fälle für die stereospezifische Polymerisation; im ersten Fall besteht eine geringe oder keine Tendenz zur Komplexbildung zwischen einem Gegenion und einem Monomersubstituenten, im zweiten findet starke Wechselwirkung zwischen Monomerem und Katalysator statt. In der ersten Gruppe wird ein stereoreguläres Polymeres nur bei niedrigen Temperaturen erhalten, in der letzteren wird aber auch bei hoher Temperatur ein hochgradig regelmässiges Polymeres erzeugt. Das Vorhandensein eines Gegenions ist notwendig, um isotaktisches Polymeres im homogenen System darzustellen und das homogene System macht die Polymerisation vorteilhafter. Die Brauchbarkeit der getroffenen Einteilung wird an der Polymerisation von Vinyläthern, Styrol, und Methylmethacrylat gezeigt. Es ist jedoch gegenwärtig noch nicht klar, warum unter der Bedingung einer Komplexbildung zwischen Gegenion und Monomersubstituenten stereoreguläres Polymeres entsteht.

Discussion

D. Braun (*Darmstadt, Allemagne*): I would like to mention that in the case of butyllithium polymerization of styrene your results are in agreement with our own work (D. Braun, W. Betz, and W. Kern, *Makromol. Chem.*, **42**, 89 (1960). In homogeneous medium we obtained tactic cristallizable polystyrene at temperatures of −30°C. and below. With increasing temperature the amount of cristallizable polystyrene decreases rapidly. The molecular weight of our polymers are rather low; which magnitude of molecular weight is obtained in your experiments?

T. Higashimura: I could not obtain a high molecular polystyrene by butyl lithium catalyst, but the molecular weight of syndiotactic poly-*i*-butyl vinyl ether was not low ($[\eta] \cong 0.8$ (100 ml./g.) in benzene at 30°C.).

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Étude de la Polymérisation Stéréospecifique de l'Isoprène par les Composés Organolithiens

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Malgré le nombre considérable de travaux consacrés à la polymérisation de l'isoprène par les organolithiens en milieu non polaire, il ne semble pas que le mécanisme de cette polymérisation soit parfaitement élucidé. Les divergences sont nombreuses entre les résultats expérimentaux publiés, et si le rôle important de l'association des extrémités lithiées est fréquemment admis, peu de données quantitatives ont été communiquées à leur sujet. Il nous a donc paru utile d'étudier cette polymérisation par des méthodes cinétiques et viscosimétriques. Ces mesures nous ont conduit à proposer un nouveau mécanisme.

Les polymérisations ont été effectuées dans le benzène et le cyclohexane. L'organolithien utilisé est l'éthyllithium.

Ce promoteur a été préparé de façon classique, par action du lithium sur le bromure d'éthyle. Le lithium est obtenu sous une forme particulièrement active par évaporation d'une solution de lithium dans l'ammoniac. L'éthyllithium formé est ensuite purifié par cristallisation.

Les différents solvants sont purifiés par addition d'éthyllithium, et distillation sur une colonne de 100 plateaux théoriques, en atmosphère d'argon.

L'isoprène est également distillé de cette façon puis prépolymérisé sur lithium et redistillé. Le solvant et le monomère sont par la suite conservés dans des tubes sous une pression de 3 kg d'argon.

La cinétique de polymérisation a été suivie au moyen d'un dilatomètre (Fig. 1) composé d'un autoclave en acier inoxydable d'un volume de 60 cc cm^3 muni d'un agitateur magnétique. Il est surmonté d'un capillaire, fixé au moyen d'un presse étoupe à bague de téflon permettant un changement rapide de ce capillaire. Trois robinets, fixés latéralement au niveau de l'agitateur, servent à introduire les différents réactifs. La purge de l'autoclave est réalisée par le capillaire au moyen d'une pompe à palette et d'une pression de 3 kg d'argon spécialement purifié. La solution de monomère est introduite jusqu'à un niveau visible dans le capillaire. Le catalyseur est ensuite ajouté en utilisant ce dernier comme burette. Nous avons employé le plus souvent une concentration en monomère de 1 mole par litre.

Il était nécessaire, pour préciser le mécanisme de l'initiation, d'étudier séparément l'étape de propagation dans les mêmes conditions. Nous avons

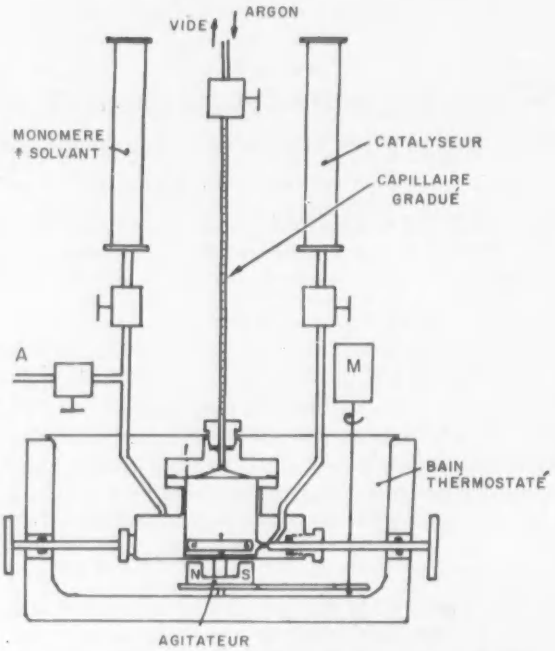

Fig. 1. Schéma du dilatomètre utilisé pour les mesures cinétiques.

donc préparé une solution de polyisoprényllithium dans le cyclohexane, par addition progressive à 90°C d'isoprène à une solution de butyllithium. Cet oligomère nous a ensuite servi à démarrer la polymérisation d'une solution molaire d'isoprène dans le cyclohexane. Les vitesses de polymérisation ont été mesurées dans un domaine de température s'étendant de 0° à 40°C, et pour des concentrations en catalyseur allant de 10^{-4} mole/l à 3×10^{-3} mole/l. Les courbes expérimentales permettent de calculer la quantité $\log [M_0]/[M]$ que l'on porte en fonction du temps. La relation obtenue est linéaire, ce qui correspond à l'équation de propagation bien connue:

$$M_xRLi + M \xrightarrow{K_p} M_{x+1}RLi \tag{1}$$

d'où

$$-d[M]/dt = K_p\,[M_xRLi][M] \tag{2}$$

et

$$\log [M_0]/[M] = K_p[M_xRLi]t = K_pCt \tag{3}$$

La vitesse de propagation sera caractérisée par la quantité $V = K_pC$. Les résultats obtenus montrent que la vitesse de propagation est directement proportionnelle à la racine carrée de la concentration en chaînes ac-

tives, c'est-à-dire qu'elle est d'ordre $^1/_2$ par rapport à ces chaînes. Ces résultats vérifient les données de Morton[1] sur l'isoprène et le butadiène ainsi que celles de Bywater[2] pour le styrène. Ce résultat s'explique en supposant une association d'ordre 2 entre les chaînes, seules les molécules dissociées participent à la polymérisation:

$$2\text{MRLi} \overset{K_1}{\rightleftharpoons} (\text{MRLi})_2 \tag{4}$$

d'où, aux fortes concentrations

$$\text{MRLi} = (C_0/2K_1)^{1/2} \tag{5}$$

$$V = K_p(C_0/2K_1)^{1/2} \tag{6}$$

On peut mesurer $K_p/(2K_1)^{1/2}$ (Tableau I). L'énergie d'activation de cette propagation peut être calculée à partir de la pente de la droite $\log (K_p/2K_1)^{1/2}] = f(1/T)$. Elle est de 19 Kcal dans le cyclohexane.

TABLEAU I

T, °C.	$(K_p/(2K_1)^{1/2}$ $\text{min}^{-1}\,\text{m}^{-1/2}\,\text{L}^{1/2}$
15	4×10^{-2}
20	$7{,}7 \times 10^{-2}$
30	$16{,}9 \times 10^{-2}$
40	46×10^{-2}

Lors de la polymérisation de l'isoprène par l'éthyllithium, nous avons en présence, pendant toute la phase d'initiation, un mélange en quantité variable de chaînes polyisoprèniques et de catalyseur non consommé. Nous nous sommes proposés d'étudier l'influence de cet excès de catalyseur sur la vitesse de polymérisation, en initiant celle-ci par des mélanges connus de polyisoprényllithium et d'éthyllithium. Deux séries de mesures ont été effectuées.

Dans la première série une quantité connue de polyisoprényllithium sert à initier la polymérisation d'une solution d'isoprène dans le cyclohexane à 15°C. La vitesse de polymérisation est suivie dilatométriquement pendant quelques minutes, puis l'on ajoute à plusieurs reprises des quantités connues d'éthyllithium, en notant à chaque fois la vitesse. Ces différentes mesures sont faites suffisamment rapidement, et la température est assez basse pour que la quantité d'éthyllithium qui entre en réaction avec l'isoprène puisse être considérée comme négligeable.

Dans la deuxième série de mesures c'est au contraire l'éthyllithium qui est introduit en premier, le polyisoprényllithium est ensuite ajouté progressivement. Le Tableau II résume différents résultats obtenus. Ces données sont représentées graphiquement sur les Figures 2–4. Sur la Figure 2 nous avons porté la vitesse en fonction de la concentration en éthyllithium pour trois concentrations en polyisoprényllithium au départ. La Figure 3 représente l'inverse de la vitesse V en fonction de la concentra-

TABLEAU II

Expt. no.	Ethyllithium, mole/l × 10^4	Polyisoprenyllithium, mole/l. × 10^4	V, min.$^{-1}$ × 10^4	$1/V$	[RLi]/[MRLi]
1	13,5	16,35	8,07	1238	0,826
		22,85	10,35	967	0,591
		32	14,4	695	0,424
		41,1	17,3	578	0,33
2	26,5	16,1	3,8	2630	1,647
		23,75	5,5	1828	1,16
		31,16	6,9	1450	0,85
		39,2	9,47	1055	0,676
		48	11,4	877	0,552
3	41,2	18,4	3,1	3225	2,24
		29,3	4,82	2075	1,405
		38	6,2	1622	1,085
		47,8	7,93	1260	0,862
4	0	C_4	20	500	
	6,25		17,4	574	
	13,75		15,6	641	
	23,7		13,2	758	
5	0	C_5	17,6	568	
	12,5		7,95	1258	
	30		3,74	2120	
6	0	C_6	13,2	758	
	6,38		8,15	1227	
	13		5,28	1894	
	19,2		4,15	2410	

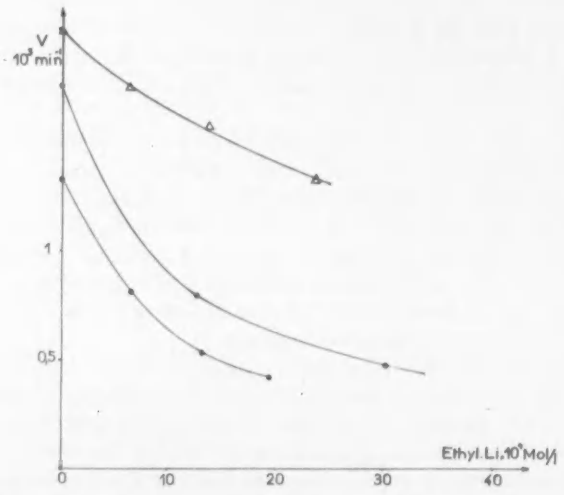

Fig. 2. Cinétique de la polymérisation de l'isoprène par un mélange d'éthyllithium et de polyisoprénylithium: (●); (○); (△); exp 6, 5, et 9.

tion en éthyllithium pour trois concentrations en polyisoprényl-Li au départ. La relation obtenue est linéaire. Sur la Figure 4 la vitesse de polymérisation est portée en fonction de la concentration en polyisoprényllithium pour trois concentrations d'éthyllithium au départ. La relation

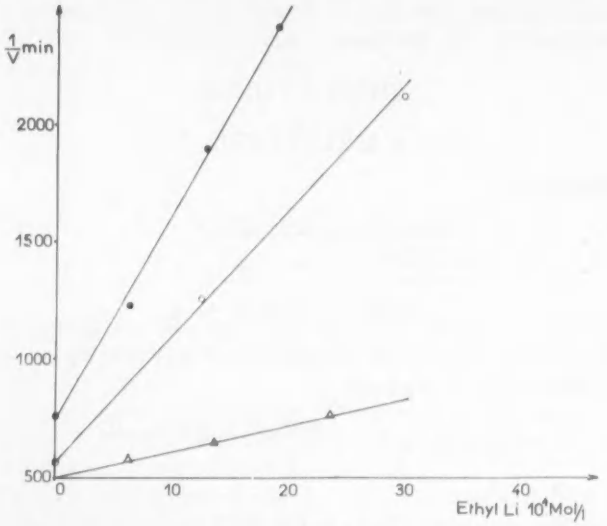

Fig. 3. Cinétique de la polymérisation de l'isoprène par un mélange d'éthyllithium et de polyisoprényllithium: (●); (○); (△); exp 6, 5, et 9.

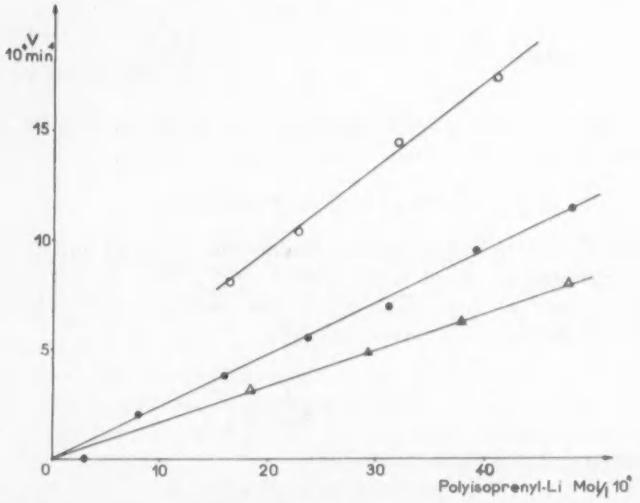

Fig. 4. Cinétique de la polymérisation de l'isoprène par un mélange d'éthyllithium et de polyisoprényllithium: (○); (●); (△); exp 1, 2, et 3.

obtenue est également linéaire et passe par l'origine dans les deux cas où la quantité d'éthyllithium est suffisamment importante.

On remarque donc que l'addition d'un organolithien diminue la vitesse de polymérisation c'est-à-dire qu'une partie des centres actifs se trouve bloquée. Ce résultat peut être expliqué en considérant une association des chaînes actives entre elles et avec l'éthyllithium, cette association étant toujours d'ordre 2. En effet des deux équilibres suivants:

$$2\mathrm{MRLi} \overset{K_1}{\rightleftharpoons} (\mathrm{MRLi})_2 \tag{7}$$

$$\mathrm{RLi} + \mathrm{MRLi} \overset{K_2}{\rightleftharpoons} (\mathrm{MRLi, RLi}) \tag{8}$$

nous déduisons:

$$[\mathrm{MRLi, RLi}]/[\mathrm{RLi}][\mathrm{MRLi}] = K_2 \tag{9}$$

et

$$[(\mathrm{MRLi})_2]/[\mathrm{MRLi}]^2 = K_1 \tag{10}$$

Si C est la concentration totale en chaînes actives et [RLi] la concentration en éthyllithium libre nous aurons:

$$(\mathrm{MRLi})_2 = \frac{C - [\mathrm{MRLi}] - [\mathrm{MRLi, RLi}]}{2} \tag{11}$$

d'où

$$2K_1[\mathrm{MRLi}]^2 + [\mathrm{MRLi}](1 + K_2[\mathrm{RLi}]) - C = 0 \tag{12}$$

et

$$[\mathrm{MRLi}] = \frac{1 + K_2[\mathrm{RLi}]}{4K_1} \left\{ \sqrt{1 + \frac{8K_1C}{(1 + K_2[\mathrm{RLi}])^2}} - 1 \right\} \tag{13}$$

Nous pouvons simplifier cette expression dans le cas où $(1 + \mathrm{K_2[RLi]})^2$ est grand devant $8K_1C$. Dans ces conditions nous avons:

$$[\mathrm{MRLi}] = C/(1 + K_2[\mathrm{RLi}]) \tag{14}$$

Si l'on fait l'hypothèse que seule les chaînes non associées sont des centres actifs cinétiques la vitesse mesurée est $V = K_p[\mathrm{MRLi}]$. Ces hypothèses rendent compte de façon satisfaisante des résultats expérimentaux précédemment décrits. Nous avons en effet:

$$V = \frac{K_p}{1 + K_2[\mathrm{RLi}]} C \tag{15}$$

qui correspond à la Figure 4, et

$$\frac{1}{V} = \frac{1}{K_pC} + \frac{K_2}{K_pC} [\mathrm{RLi}] \tag{16}$$

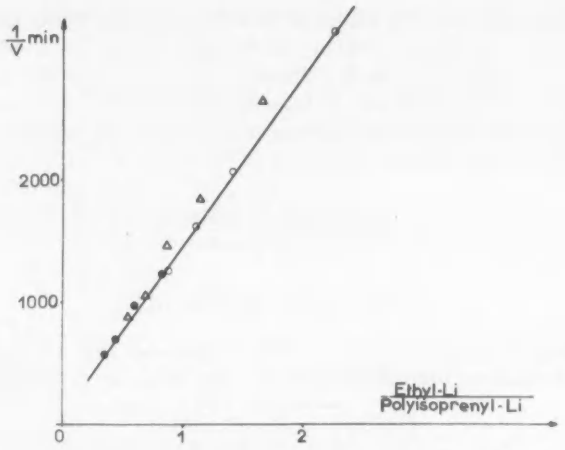

Fig. 5. Cinétique de la polymérisation de l'isoprène par un mélange d'éthyllithium et de polyisoprénylithium: (○); (●); (△); exp 1, 2, et 3.

représenté sur la Figure 3. En portant V^{-1} en fonction du rapport entre éthyllithium et polyisoprénylithium nous obtenons une droite dont la pente nous donne la valeur du rapport K_2/K_p (Fig. 5).

Cette valeur est trouvée égale à 1380 à 15°C. En combinant les valeurs obtenues pour $q = K_p/(1 + K_2[\text{RLi}])$ et K_2/K_p nous pouvons calculer K_p et K_2 (Tableau III): $K_p = 1{,}8$ et $K_2 = 2480$.

TABLEAU III

Expt. no.	Ethyllithium, mole/l. × 10^3	q	K_p
152	2,65	0,24	1,93
153	4,12	0,16	1,72
		Moyenne	1,8

L'étude que nous avons faite sur la cinétique de propagation nous a permis de mesurer la vitesse $K_p[\text{MRLi}]$ à la même température.

Les mesures cinétiques nous donnent la valeur de $K_p/(2K_1)^{1/2}$. A 15°C cette valeur est égale à 4×10^{-2}. Avec la valeur de K_p mesurée précédemment nous déduisons $K_1 = 10^3$.

La valeur de cette constante apparaît faible, si on la compare a l'ordre $^1/_2$ observé pour la cinétique de propagation jusqu'à des concentrations en catalyseur inférieures à 10^{-4} mol/l. Il est donc vraisemblable, que l'équilibre thermodynamique ne se rétablit pas instantanément entre les différents composés lithiés, lorsque l'on modifie la composition du mélange.

Apres avoir étudié la polymérisation de l'isoprène directement initiée par des chaînes actives, puis par des mélanges d'éthyllithium et de chaînes

actives, nous avons suivi la cinétique de polymérisation initiée par l'éthyllithium seul. Une étude complète de cette polymérisation a été effectuée à différentes températures et à différentes concentrations en catalyseur, dans deux solvants: le benzene et le cyclohexane.[4] Nous ne considérerons ici que quelques résultats confirmant directement nos précédentes hypothèses.

$$\mathrm{RLi} + \mathrm{M} \xrightarrow{K_i} \mathrm{MRLi} \tag{17}$$

d'où

$$d[\mathrm{MRLi}]_t/dt = K_i[\mathrm{RLi}][\mathrm{M}] \tag{18}$$

ou $[\mathrm{MRLi}]_t$ est la concentration totale en polyisoprényl Li et [RLi] est la concentration en organolithien libre. Au début de la polymérisation:

$$[\mathrm{MRLi}]_t = K_i[\mathrm{RLi}][\mathrm{M}_0]t \tag{19}$$

En tenant compte de la formule (14) nous obtenons:

$$[\mathrm{MRLi}] = \frac{K_i[\mathrm{RLi}][\mathrm{M}_0]}{1 + K_2[\mathrm{RLi}]}t \tag{20}$$

et si $K_2[\mathrm{RLi}]$ est grand devant eq. (1)

$$[\mathrm{MRLi}] = \frac{K_i[\mathrm{M}_i]}{K_2}t \tag{21}$$

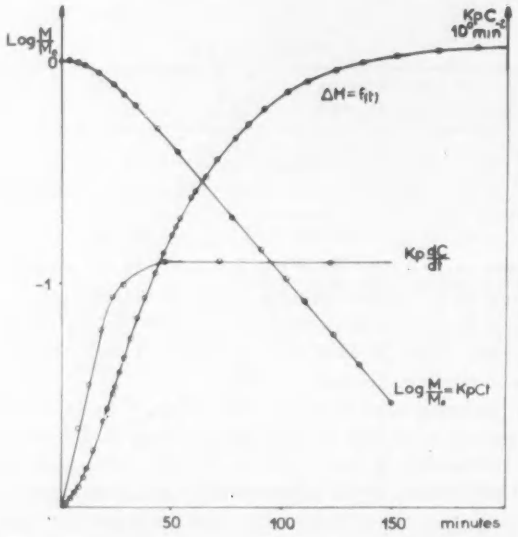

Fig. 6. Exemple de courbes obtenues lors de la polymérisation de l'isoprène par l'éthyllithium.

la vitesse de formation des centres actifs cinétiques sera donc indépendante de la concentration en éthyllithium.

De la courbe cinétique expérimentale de consommation du monomère nous déduisons la courbe log $[M_0]/[M] = K_p[MRLi]t$. La pente à l'origine de la courbe dérivée de celle-ci par rapport au temps nous donne la valeur de $p = K_p d[MRLi]/dt$ au temps O. La Figure 6 donne un exemple de ces courbes.

Cette valeur p a été mesurée pour différentes concentrations en catalyseur. Le solvant utilisé était le cyclohexane et la température 15°C (Fig. 7).

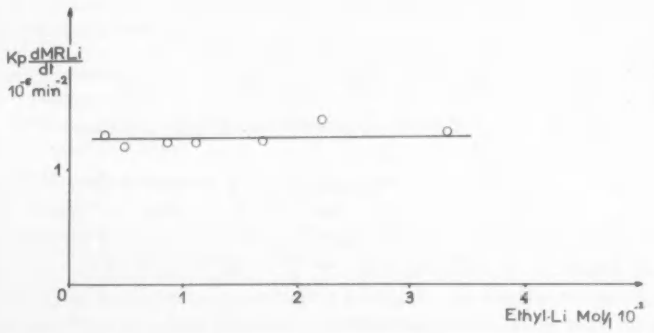

Fig. 7. Vitesse de formation de centres actifs cinétiques dans la polymérisation de l'isoprène par l'éthyllithium.

Nous voyons effectivement que dans un domaine de concentration allant de 2×10^{-3} à $3,4 \times 10^{-2}$ mole/l en éthyllithium la vitesse de formation des centres actifs cinétiques est sensiblement constante. Ceci explique également le palier observé pour les vitesses de polymérisation à partir de 2×10^{-3} mole/l. Les valeurs de p ont été déterminées à différentes températures pour une même concentration en éthyllithium de 10^{-2} mole/l en utilisant le benzène et le cyclohexane comme solvant. En portant le logarithme de ces valeurs en fonction de l'inverse de la température absolue qui leur correspond nous obtenons une droite dont la pente nous permet de calculer l'énergie d'activation globale qui préside à la formation des centres actifs cinétiques (Fig. 8)

D'après le mécanisme précédent

$$p = (K_p K_i / K_2)[M_0] \qquad (22)$$

L'énergie d'activation mesurée sera la somme des energies correspondant à $K_p K_i$ et K_2. L'énergie d'activation mesurée pour la propagation correspond à $K_p/(2K_1)^{1/2}$. Des mesures viscosimétriques que nous avons effectuées sur des solutions diluées de polyisoprénylllithium tendent à montrer que l'énergie d'activation correspondant à l'équilibre de dimérisation des chaînes actives entre elles et avec l'éthyllithium est faible.[5] En

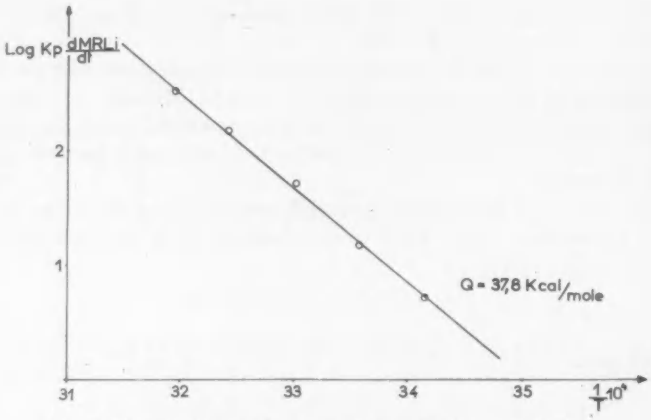

Fig. 8. Energie d'activation mesurée pour la phase d'initiation.

les négligeant nous déduisons des valeurs de p mesurées dans le benzène $Q_p + Q_i = 38$ Kcal. L'énergie d'activation Q_p dans le benzène a été trouvée égale à 16 Kcal. Il reste donc $Q_i = 22$ Kcal. Dans le cyclohexane on a de même $Q_p = 19$ Kcal et $Q_p + Q_i = 46$ Kcal, d'où $Q_i = 27$ Kcal.

Pour rendre compte des résultats précédents il n'est donc pas nécessaire de faire intervenir une association de l'éthyllithium ni une association d'ordre supérieur à 2 pour le polyisoprényllithium. Une autre confirmation de ces hypothèses a été trouvée dans des études viscosimétriques que nous avons effectuées sur des solutions de polyisoprényllithium dans le cyclohexane. Morton a déjà signalé à la suite d'études sur des solutions très concentrées une baisse importante de viscosité lorsque l'on détruit les extremités lithium des chaînes polymériques. Cette chute de viscosité correspond à une association d'ordre 2 entre ces chaînes. Ce même auteur a mesuré également la chute de viscosité produite par l'addition d'une solution de butyllithium à une solution de polyisoprényllithium ce qui implique l'intervention du butyllithium dans l'équilibre d'association des chaînes polymériques. Par ailleurs ces résultats ne sont cohérents que si l'on suppose une dissociation du butyllithium, à ces concentrations, ce qui semble confirmé par les travaux de Rodionov.[4] Nous avons repris ces différentes mesures en utilisant des solutions suffisamment diluées pour que les lois classiques de la viscosimétrie soient appliquables.[5] Elles confirment l'association d'ordre 2 déjà signalée entre les chaînes. Par addition de solutions, dans le cylohexane, de butyllithium et d'éthyllithium à des solutions de polyisoprényllithium nous avons mesuré les constantes d'équilibre correspondant à:

$$(\mathrm{MRLi})_2 + 2\mathrm{RLi} \overset{K_3}{\rightleftharpoons} 2(\mathrm{MRLi}, \mathrm{RLi}) \qquad (23)$$

Cette constante K_3 semble être plus forte pour l'éthyllithium que pour le butyllithium. Or les trois constantes K_1, K_2, et K_3 sont liées par la relation

$K_1K_2 = K_2^2$. K_2 est donc plus grand pour l'éthyllithium que pour ln butyllithium ce qui explique la vitesse d'initiation plus faible avec le premier catalyseur.

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Résumé

Nous avons étudié la cinétique de la polymérisation de l'isoprène en milieu non polaire en utilisant successivement comme initiateur, le polyisoprényllithium, des mélanges de polyisoprényllithium et d'éthyllithium, et l'éthyllithium seul. Les résultats obtenus montrent le rôle important joué pendant l'initiation par l'équilibre d'association entre les chaînes polymériques et le catalyseur non consommé. L'étude viscosimétrique de solutions diluées de mélanges de polyisoprényllithium et de mélanges d'éthyllithium corroborent le mécanisme proposé.

Synopsis

We have studied the polymerization kinetics of isoprene in nonpolar media, using as initiator either ethyllithium or polyisoprenyllithium or mixtures of them both. It appears, from our series of experiments, that the association equilibrium between unused catalyst and growing polymeric chain is of great importance during the initiation process. The proposed kinetic scheme is supported satisfactorily by the results of viscometric determinations on dilute solutions of mixtures of polyisoprenyllithium and ethyllithium.

Zusammenfassung

Die Kinetik der Polymerisationsreaktion des Isoprens in unpolaren Lösungsmitteln wurde in der vorliegenden Arbeit unter der Einwirkung von Äthyllithium oder von Polyisoprenyllithium oder von der Mischung derbeiden, studiert. Die Ergebnisse, die wir erhielten, deuten darauf hin, dass die Assoziationsgleichgewichte zwischen dem unverbrauchten Initiator und den Machsenden Polymerketten eine hervorragende Rolle während des Initiations-vorganges spielen. Der vorgeschlagene kinetische Mechanismus ist von den Ergebnissen der Viskositätsmessungen, die wir an verdünnten Lösungen von Polyisoprenyllithium-Äthyllithium-Mischungen durchgeführt haben, bestätigt.

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Quelques Types Particuliers de Catalyseurs au Cobalt dans la Polymérisation du Butadiène

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Du polybutadiène à haute pureté a été obtenu[1] et caractérisé[2] par Natta, en enrichissant par des cristallisations fractionnées des polymères obtenus avec des catalyseurs à base de chlorures de titane.

Des catalyseurs à base d'iodures de titane, capables de produire directement des polybutadiènes ayant une haute teneur en enchaînements 1,4-*cis*, ont été découverts par des chercheurs de la Phillips Petroleum Co.[3] Un autre groupe de catalyseurs a été ensuite découvert et décrit, par nous[4,5] et par d'autres chercheurs.[6,7] Ces catalyseurs, qui sont constitués par l'association de composés du cobalt avec des halogénures d'aluminium-alcoyle, agissent en phase homogène et sont très stéréospécifiques puisqu'ils peuvent produire du polybutadiène 1,4-*cis* ayant un titre même supérieur à 99%. Au contraire, l'association de composés du cobalt avec des aluminium-trialcoyles donne lieu, toujours avec une très haute stéréospécificité, à la formation du polybutadiène-1,2 syndyotactique.[8]

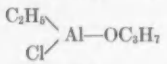
Dans cet exposé, nous avons décrit les résultats d'une série d'expériences sur la polymérisation du butadiène, conduites avec des catalyseurs à base de composés du cobalt et de composés aluminium-alcoylés d'un type particulier, obtenus en substituant l'une des liaisons Al—C d'un aluminium-trialcoyle ou d'un halogénure d'aluminium-dialcoyl avec des liaisons Al—O ou bien Al—N.

L'emploi de ces catalyseurs dans la polymérisation du butadiène détermine, dans la marche de la réaction et dans les caractéristiques des polymères, des variations sensibles dont la connaissance contribue à l'interprétation du mécanisme de cette catalyse.

RÉSULTATS

a. Préparation

Nous avons préparé une série de composés aluminium-alcoylés caractérisés par la présence d'une liaison Al—O ou bien Al—N, et précisément les composés (I–IX).



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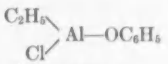

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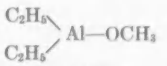

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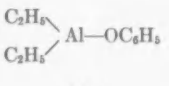

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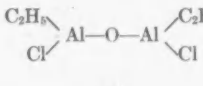

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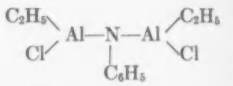

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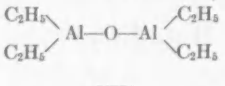

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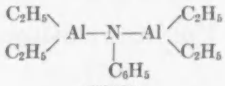

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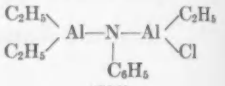


(IX)

Nous avons obtenu ces composés par les méthodes suivantes:

Alcoolates et Phénates d'Aluminium-diéthyle et de Aluminium-monochloromonoéthyle (I, II, III, IV). Ils ont été préparés en faisant réagir, à la température ambiance, des solutions benzéniques contenant 10% de $Al(C_2H_5)_3$ ou bien respectivement de $Al(C_2H_5)_2Cl$ avec les quantités stoéchiométriques des alcools méthylique, *n*-propylique et du phénol (ce dernier dissous dans le benzène). On a utilisé directement les solutions après avoir contrôlé leur teneur en alcoolate par la méthode de Skrabal.[9]

Composés à Pont d'Oxygéne (V et VII). Dans une solution saturée d'eau en benzène (0,4 g/l), on injecte rapidement, au moyen d'une pipette à seringue, une solution benzénique de $Al(C_2H_5)_3$ ou bien de $Al(C_2H_5)_2Cl$ à 10%. L'eau et le composé aluminium-alcoylé sont en rapport molaire 1:2.

Au moment ou l'on ajoute l'aluminium-alcoyle au benzène humide, on observe un léger développement de chaleur en même temps que de gaz (éthane). La solution reste parfaitement limpide.

Il est nécessaire d'opérer suivant la méthode énoncée afin d'éviter la formation d'hydrate d'aluminium insoluble.

La solution ainsi obtenue est concentrée en évaporant le benzène y contenu sous vide partiel. Le composé qui se forme à partir de $Al(C_2H_5)_3$ est presque sûrement le $(C_2H_5)_2$ Al—O—$Al(C_2H_5)_2$. De toute façon, ce composé n'a pas été isolé et on s'est limité à déterminer dans la solution, le rapport Al/C_2H_5, qui est résulté égal à 0,52.

Au contraire, à partir de $Al(C_2H_5)_2Cl$, on a évaporé complètement le benzène et on a soumis le produit obtenu à une distillation sous vide poussé.

A 38–40°C et 0.001 mm Hg, on a obtenu un liquide limpide, mobile, incolore, qui réagit violemment avec l'air et l'humidité. L'analyse a donné les résultats.

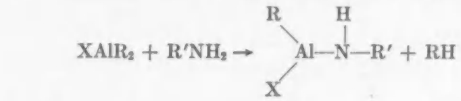
TABLEAU I

	Composition expérimentale, %	Composition calculée, %
Al	26.20	27.11
Cl	36.85	35.64
C_2H_5	28.90	29.21
O	8.05 (par différence)	8.04

(Tableau I) qui correspondent à la formule $(C_2H_5)Cl$ Al—O—$AlCl(C_2H_5)$.

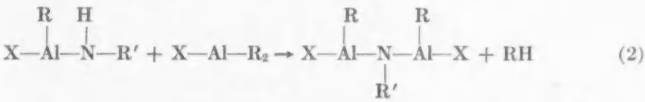
La teneur en C_2H_5 a été déterminée par la méthode volumétrique gazeuse.[10]

Composés à Pont d'Azote (VI et VIII). A une température inférieure à 100 °C, la réaction entre une amine primaire et $Al(C_2H_5)_3$ ou bien $Al(C_2H_5)_2Cl$ donne lieu à la substitution d'un seul atome d'hydrogène de l'amine:



$$XAlR_2 + R'NH_2 \rightarrow \begin{matrix} R & H \\ \diagdown & | \\ Al & -N-R' \\ | & \\ X & \end{matrix} + RH \qquad (1)$$

Si, au contraire, on réchauffe au delà de 100 °C, on réussit à substituer aussi le deuxième hydrogène:



$$\begin{matrix} R & H \\ | & | \\ X-Al-N-R' \end{matrix} + X-Al-R_2 \rightarrow \begin{matrix} & R & & R & \\ & | & & | & \\ X-Al-N-Al-X & + & RH \\ & | & & & \\ & R' & & & \end{matrix} \qquad (2)$$

Ces deux réactions peuvent être suivies très aisément en mesurant le gaz (C_2H_6) qui se forme durant les réactions mêmes.

Par cette méthode, nous avons préparé les composés (VI) et (VIII) en faisant réagir l'aniline et $Al(C_2H_5)_3$ ou bien $Al(C_2H_5)_2Cl$ en rapport molaire 1:2; operant avec le benzène à sa température d'ébullition, la réaction (1) s'est produite. Une fois que la quantité théorique de gaz s'est développée, on a évaporé sous vide le benzène et on l'a substitué avec du xylène: en réchauffant jusqu'à la température d'ébullition (135–140 °C) pendant 10 heures, réaction (2) s'est developpée.

Le gaz total dégagé correspondait à la quantité théorique et était constitué par de l'éthane.

Les solutions xyléniques ainsi obtenues, d'une couleur jaune pâle, avaient le comportement typique des solutions des composés aluminium-alcoylés.

L'analyse, effectuée sur les solutions xyléniques, a mis en évidence dans le composé (VI) un rapport $Al:Cl:N:C_2H_5 = 1:1:0{,}5:1{,}05$. Dans le composé (VIII) le rapport est resulté $Al:N:C_2H_5 = 1:0{,}48:1{,}98$.

Composé IX. Suivant ce que nous avons exposé précédemment, ce composé a été préparé en faisant réagir dans le benzène, l'aniline avec $Al(C_2H_5)_2Cl$ en rapport 1:1. Après 5 h 30′ d'ébullition, la quantité théorique de gaz s'est développée. On a donc substitutué le benzène avec du xylène et on a ajouté $Al(C_2H_5)_3$ en rapport 1:1 avec les autres réactifs. Après 5 heures d'ébullition, le gaz développé correspondait à la quantité théorique et il était constitué par de l'éthane.

Le composé a été utilisé directement dans la solution xylénique. L'analyse indiquait un rapport $Al:Cl:N:C_2H_5 = 1:0{,}51:0{,}5:1{,}47$.

b. Polymérisation

Les aluminium-alcoyles ainsi obtenus, ont été employés dans la préparation de catalyseurs pour la polymérisation du butadiène, en les associant à des composés ou à des complexes du cobalt, (Co^{II} acétylacétonate; $CoCl_2$·

TABLEAU II

Essai no.	Composé organométallique: Types	Moles × 10^2	$CoCl_2 \cdot 2$ Py, moles × 10^5	Benzène, ml	Temp. réaction, °C	Durée réaction, h	Polymère obtenu, g	Conversion, %
1	$AlEt_2Cl$	2.0	9.23	500	15	2	48.9	97.8
2	$Et_2Al—OC_6H_5$ (Et, Cl)	2.06	9.23	500	15	10.5	Traces de polymère huileux	—
3	$Et_2Al—OC_3H_7$ (Et, Cl)	4.08	9.23	500	15	11	Traces de polymère huileux	—

TABLEAU III

Essai no.	Composé organométallique: Type	Moles × 10^2	$CoCl_2 \cdot 2$ Py, moles × 10^5	Benzène, ml	Temp. réaction, °C	Durée réaction, h	Polymère obtenu, g	Conversion, %
4	$AlEt_3$	2.28	7.7	500	15	9	15[a]	30
5	Et_2AlOCH_3	2.02	7.7	500	15	9.5	Traces	—
6	$Et_2AlOC_6H_5$	2.6	7.7	500	15	9	Traces	—

[a] 1,2 Syndyotactique, crist. 75%.

TABLEAU IV

Essai no.	Composé organométallique		Sel de cobalt		Benzène, ml	Temp. réaction, °C	Durée, h	Polymère obtenu, g	Conversion, %	$M \times 10^{-3}$	Gel, %	Examen infra-rouge		
	Type	Moles $\times 10^2$	Type	Moles $\times 10^5$								1,4-*cis*, %	1,4-*trans*, %	1,2, %
7	$(EtClAl)_2O$	1.26	$CoCl_2 2Py$	9.23	500	15	2.75	22.3	99.9	232	0	97.6	1.1	1.3
8	$(EtClAl)_2O$	1.26	$CoCl_2 2Py$	7.7	500	15	2.75	21	87.5	286	0	97.5	1.1	1.4
9	$(EtClAl)_2O$	1.26	$CoCl_2 2Py$	7.7	500	15	2.75	31.2	97.3	352	1	96.9	1.5	1.6
10	$AlEt_2Cl$	1.45	$CoCl_2 2Py$	7.7	500	15	1.16	30	100	190	0.5	97.3	1.2	1.5
11	$(EtClAl)_2O$	1.26	Co(acétylacétonate)$_2$	6.15	500	15	4.5	26	81.2	487	1.5	96.7	1.9	1.4
12	$AlEt_2Cl$	1.45	Co(acétylacétonate)$_2$	6.15	500	15	1.33	25	96.2	212	0	97	1.2	1.8
13	$(EtClAl)_2O$	1.26	Co(acétylacétonate)$_2$	7.7	500	15	7.5	39.5	79	454	2.5	96.9	1.4	1.7
14	$AlEt_2Cl$	1.45	Co(acétylacétonate)$_2$	7.7	500	15	1.5	38	95	242	3.0	96.8	1.4	1.8

TABLEAU V

Essai no.	Composé organométallique		Sel de cobalt		Benzène, ml	Temp. réaction, °C	Durée réaction, h	Polymère obtenu, g	Conversion, g	$M \times 10^{-3}$	Gel, %	Examen infra-rouge		
	Type	Moles $\times 10^2$	Type	Moles $\times 10^5$								1,4-*cis*, %	1,4-*trans*, %	1,2, %
15	$\left(\begin{matrix}Et\\Cl\end{matrix}\!\!>\!Al\right)_2NC_6H_5$	1.83	$CoCl_2 2Py$	10.8	500	15	7.5	21.3	97	189	1	97	1.4	1.6
16	$\left(\begin{matrix}Et\\Cl\end{matrix}\!\!>\!Al\right)_2NC_6H_5$	1.24	$CoCl_2 2Py$	7.7	500	15	10.75	18	75	235	0	96.6	1.4	2.0
17	$\left(\begin{matrix}Et\\Cl\end{matrix}\!\!>\!Al\right)_2N_6CH_5$	1.83	$CoCl_2 2Py$	9.23	500	15	8	35.2	94.6	387	0	97.1	1.5	1.4
18	$AlEt_2Cl$	1.45	$CoCl_2 2Py$	9.23	500	15	2	36	100	197	1	96.7	1.3	2.0
19	$\left(\begin{matrix}Et\\Cl\end{matrix}\!\!>\!Al\right)_2NC_6H_5$	1.83	Co(acétyl-acétonate)$_2$	9.23	500	15	9.75	40	91	450	0	96.6	1.8	1.6
20	$AlEt_2Cl$	1.45	Co(acétyl-acétonate)$_2$	9.23	500	15	2.5	39.5	98.7	217	0.5	96.9	1.1	2.0
21	$\left(\begin{matrix}Et\\Cl\end{matrix}\!\!>\!Al\right)_2NC_6H_5$	1.83	Co(acétyl-acétonate)$_2$	9.23	500	15	10	47	94	515	1	96.6	1.9	1.5
22	$AlEt_2Cl$	1.45	Co(acétyl-acétonate)$_2$	9.23	500	15	2.75	47.2	98.2	259	0	97	1.3	1.7

TABLEAU VI

Essai no.	Composé organométallique Type	Moles × 10^2	$CoCl_2 \cdot 2Py$, moles × 10^5	Benzène, ml	Temp. réaction, °C	Durée, h	Polymère obtenu, g	Conversion %	Examen moyen de rayons-X Constitution	Cristallinité, %
23	$(Et_2Al)_2O$	1.77	7.7	1000	15	2	45	45.5	1,2 syndiotactique	78
24	$(Et_2Al)_2O$	1.77	6.15	1000	15	5	55	52.5	1,2 syndiotactique	75
25	$(Et_2Al)_2O$	2.18	7.7	1000	15	6.5	70	70	1,2 syndiotactique	68.4
26	$(Et_2Al)_2NC_6H_5$	1.54	9.23	1000	15	9	8	26	1,2 syndiotactique	66.2

TABLEAU VII

Essai no.	Et_2Al | N—AlEtCl, | C_6H_5 moles × 10^2	$CoCl_2 \cdot 2Py$, moles × 10^5	Benzène, ml	C_4H_8, g	Conversion, %	Cristallinité du polymère brut, %	Extraction par le benzol: Extrait, %	Résidu, %	Extrait benzolique: 1,4-*cis*, %	1,4-*trans*, %	1,2, %	$[\eta]$	$M \times 10^{-3}$	Cristallinité du résidu à l'extraction, %
27	1.83	7.7	500	52	75	17.2	49.6	50.4	90.9	4.0	5.1	0.95	57.5	54.4 (1,2 syndiotactique)
28	1.83	10.8	500	35	44.3	22.5	31.3	68.7	89.3	4.2	6.5	0.52	27	71.1 (1,2 syndiotactique)

2 C_5H_5N) solubles dans le solvant utilisé pour la réaction (benzène). Les méthodes operatiores, la concentration des divers réactifs et les conditions de réaction adoptées, sont les mêmes que celles deja utilisées avec des résultats satisfaisants, dans la préparation du polybutadiène 1,4-*cis* et 1,2 syndyotactique, par les catalyseurs ordinaires à base de composés du cobalt et de $Al(C_2H_5)_2Cl$ ou respectivement de $Al(C_2H_5)_3$.

Tout d'abord, on a expérimenté les composés (I) et (II), obtenus de $Al(C_2H_5)_2Cl$ par substitution d'un groupe alcoylé avec un groupe oxyalcoylé ou bien oxyarylé. Ils se sont démontrés incapables de donner lieu à des catalyseurs actifs dans la polymérisation du butadiène (dans le Tableau II les expériences effectuées avec ces catalyseurs sont comparées à une autre, tout à fait égale mais dans laquelle on a employé $Al(C_2H_5)_2Cl$).

Un résultat similaire a été obtenu avec des catalyseurs préparés en utilisant les composés (III) et (IV). Ils se sont en effet montrés, eux-aussi, incapables de polymériser le butadiène contrairement à ce qui se vérifie dans les mêmes conditions, avec un catalyseur du même type préparé en utilisant $Al(C_2H_5)_3$ (Tableau III).

Des résultats tout à fait différents ont été au contraire obtenus en employant les composés (V) et (VI), caractérisés par la présence d'un pont d'oxygène ou bien d'azote entre les deux atomes de Al. Les catalyseurs obtenus se sont démontrés actifs et fortement stéréospécifiques dans la préparation du polybutadiène 1,4-*cis*. Dans les Tableaux IV et V on a indiqué les résultats de ces essais et d'autres, effectués dans les mêmes conditions, mais en employant $Al(C_2H_5)_2Cl$ dans la préparation du catalyseur. La comparaison entre les résultats obtenus avec les différents types de catalyseurs met en évidence des différences substantielles. Ces différences ne concernent pas le titre en 1,4-*cis*, qui se maintient très haut dans tous les cas, mais la vitesse de réaction, qui est sensiblement inférieure dans le cas des catalyseurs préparés avec les composés (V) et (VI), et surtout la masse moléculaire. En effet, les autres conditions étant les mêmes, on observe que, avec ces catalyseurs, on obtient des masses moléculaires qui sont à peu près doubles par rapport à celles obtenus dans les essais de comparaison.

Les catalyseurs constitués par des composés du cobalt associés avec les composés (VII) et (VIII) démontrent une haute activité catalytique et une importante stéréospécificité dans l'orientation de la polymérisation du butadiène vers la structure 1,2 syndyotactique; ils se comportent donc de la même façon que $Al(C_2H_5)_3$ (Tableau VI). Dans ce cas, l'insolubilité du polymère empêche de déterminer, et par conséquent de comparer, la masse moléculaire des polybutadiènes obtenus au moyen des divers catalyseurs.

Nous avons enfin expérimenté les catalyseurs au cobalt obtenus en employant un aluminium-alcoyle du type (IX), c'est-à-dire une substance qui, d'un côté ressemble aux composés du type (V) et (VI) et de l'autre à ceux du type (VII) et (VIII). Nous avons ainsi obtenu (Tableau VII) des polymères constitués par un mélange mécanique de polybutadiène-1,4-*cis*

et de polybutadiène-1,2 syndyotactique séparables, au moyen d'extraction par le benzène, en deux fractions dont chacune contient l'une des deux formes stéréoisomères à l'état presque pur.

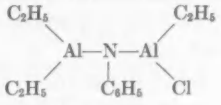
DISCUSSION

Sur la base des résultats indiqués et des connaissances précédentes, les composés aluminium-alcoylés, en ce qui concerne leur comportement dans la polymérisation du butadiène au moyen de catalyseurs au cobalt, peuvent être subdivisés en trois groupes: (1) composés qui donnent lieu à des catalyseurs capables de polymériser le butadiène dans la structure 1,4-*cis*: R_2AlCl, $RAlCl_2$, RClAl—O—AlClR, RClAl—NR—AlClR; (2) composés qui servent à préparer des catalyseurs pour polymériser le butadiène dans la structure 1,2 syndyotactique: R_3Al, R_2Al—O—AlR_2, R_2—Al—NR—AlR_2; (3) Composés qui ne donnent pas lieu à des catalyseurs actifs: R_2Al—OR ou RClAl—OR.

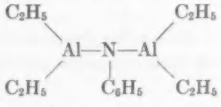
Le fait que parmi les composés aluminium-alcoylés substitués, seulement ceux à pont de O ou N donnent lieu à des catalyseurs actifs, tandis que ceux qui ont une simple liaison Al—O (ou Al—N) se démontrent inertes, doit être probablement attribué au degré d'association trop élevé de ces derniers, ce qui les rend incapables de donner lieu à la formation du complexe catalytique avec le sel de cobalt. Le haut degré d'association de ces composés est d'autre part confirmé aussi par leur absence d'activité dans la polymérisation cationique (par exemple de l'isobutène) qui est cependant catalysée par les aluminium-alcoyles à pont de O ou N.

Il est beaucoup plus difficile d'expliquer la différence de masse moléculaire des polybutadiènes 1,4-*cis*, lorsqu'on opère avec des catalyseurs préparés en utilisant les composés V et VI au lieu de $Al(C_2H_5)_2Cl$. Le fait que les poids moléculaires soient doublés presque exactement, est sans doute suggestif, mais la connaissance insuffisante de la nature du composé catalytique, du mécanisme de son action et de la cinétique de polymérisation rendent pour le moment hasardeux tout essai d'interprétation.

La capacité que les catalyseurs préparés en utilisant le composé IX ont de donner lieu en même temps à des chaînes très pures de polybutadiène soit 1,4-*cis*, soit 1,2 syndyotactique, ferait penser à la possibilité, sans doute attrayante, qu'un seul centre catalytique puisse engendrer simultanément des macromolécules de structure différente. Mais il existe le doute que, à la suite d'un échange de radicaux, le composé



puisse être transformé en un mélange de



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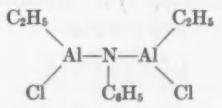

d'ou il en dériverait un mélange de deux catalyseurs divers dont chacun serait responsable de la formation d'un des deux différents types d'enchaînement.

PARTIE EXPÉRIMENTALE

Appareillage et Réactifs

Les polymérisations ont été effectuées dans des autoclaves de 1800 ml munis d'un agitateur et d'une chemise pour la circulation du fluide de thermostatation.

Les méthodes opératoires ont été semblables à celles deja connues pour ce type de polymérisations.

On a utilisé du butadiène Phillips "pure grade" et du benzène C. Erba pur, du type pour analyse, rectifié, désaéré, desseché sur Silicagel et conservé sous azote.

On a utilisé du $CoCl_2$ C. Erba pur, du type pour analyse. L'acétylacétonate de cobalt a été préparé par nous selon la méthode de Charles et Pawlikowski.[11] $Al(C_2H_5)_3$ et $Al(C_2H_5)_2Cl$, produits par la Montecatini, ont été encore rectifiés par nous.

Contrôles Analytiques

La détermination au spectrographe infra-rouge, du pourcentage des différentes structures stéréoisomères dans le polybutadiène 1,4-*cis*, a été effectuée suivant la méthode de Morero et al.[12]

Le numéro de gel a été déterminé sur la base de la partie non dissoute (résidu à la filtration sur un réseau à 6000 mailles/cm^2) dans le toluène, après 48 heures à température ambiante, sans agitation, de 0,1 g de polymère dans 40 ml de solvant. La viscosité intrinsèque a été mesurée à 26°C en solution toluénique avec un viscosimètre Desreux-Bischoff. La masse moléculaire a été déduite de la formule de Johnson et Wolfangel pour les polybutadiènes linéaires.[13]

Le pourcentage de cristallinité des polybutadiènes-1,2 syndyotactiques a été déterminé par diffraction des rayons X, à partir de la structure étudiée par Natta et al.[14]

Nous désirons remercier C. A. Ceselli et M. Camia pour les analyses au spectrographe I.R. et G. Lanzavecchia pour les déterminations par diffraction der rayons X et les mesures de viscosité.

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Résumé

On a étudié la polymérisation du butadiène avec des catalyseurs constitués par des composés au cobalt et par les composés suivants d'aluminium-alcoyles modifiés: $(EtClAl)_2O$, $(EtClAl)_2NC_6H_5$, $(Et_2Al_2)O$, $(Et_2Al)_2NC_6H_5$, $EtClAl—N(C_6H_5)—AlEt_2$, Et_2AlOR, et EtClAlOR, où R est alcoyle ou aryle. Le comportement de ces catalyseurs a été étudié soit du point de vue de la conduite de la polymérisation soit aussi en ce qui concerne la composition stéréoisomérique et les poids moléculaires des polybutadiènes obtenus. Suivant le composé aluminium-organique employé, on peut obtenir des polybutadiénes à structure essentiellement 1,4-*cis* ou 1,2 syndiotactique ou leurs mélanges. Quelques-uns de ces composés se démontrent au contraire catalytiquement inertes. Les resultats obtenus révèlent quelques aspects de la polymérisation stéréospécifique homogène du butadiène avec des catalyseurs au cobalt et peuvent aider pour la connaissance de leur nature et de leur mécanisme d'action.

Synopsis

The polymerization of butadiene in the presence of catalysts containing cobalt compounds and modified alkyl aluminum has been studied: $(EtClAl)_2O$, $(EtClAl)_2NC_6H_5$, $(Et_2Al_2)O$, $(Et_2Al)_2NC_6H_5$; $EtClAl—N(C_6H_5)—AlEt_2$, Et_2AlOR, and EtClAlOR where R = alkyl or aryl. The behavior of these catalysts has been studied from the point of view of the course of polymerization and of the stereoisomeric composition and molecular weight distribution of the polybutadienes. Depending the nature of the organoaluminum, 1-4-*cis*-polybutadienes, 1,2-syndiotactic polybutadienes and mixtures of both polymers can be obtained. Contrarily some compounds are inert catalysts. The results show some aspects of the homogeneous stereospecific polymerization of butadiene with cobalt catalysts and can be used for the interpretation of their nature and reaction mechanism.

Zusammenfassung

Die Polymerisation von Butadien mit Katalysatoren aus Kobaltverbindungen und den folgenden modifizierten Aluminum-Alkylverbindungen wurde untersucht: $(EtClAl)_2O$, $(EtClAl)_2NC_6H_5$, $(Et_2Al_2)O$, $(Et_2Al)_2NC_6H_5$, $EtClAl—N(C_6H_5)—AlEt_2$, Et_2AlOR, and $EtClAlOR$, wo R = Alkyl oder Arylist. Das Verhalten dieser Katalysatoren wurde sowohl vom Gesichtspunkt des Polymerisationsverlaufes als auch in bezug auf die Zusammensetzung der erhaltenen Polybutadiene aus Stereoisomeren und ihr Molekulargewicht untersucht. Je nach der verwendeten aluminium-organischen Verbindung kann man im wesentlichen Polybutadiene mit 1,4-*cis* oder 1,2-syndiotaktischer Struktur oder Mischungen davon erhalten. Einige dieser Verbindungen erweisen sich aber als katalytisch inert. Die erhaltenen Ergebnisse zeigen einige Aspekte der homogenen stereospezifischen Polymerisation des Butadiens mit Kobaltkatalysatoren auf und können der Kenntnis ihrer Natur und ihres Wirkungsmechanismus förderlich sein.

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Cobalt Catalysts for Preparing Syndiotactic 1,2-Polybutadiene

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The first stereoregular butadiene polymers with a 1,4 (*cis* and *trans*) and a 1,2 (isotactic and syndiotactic) structure were obtained by Natta and co-workers at the Polytechnic Institute of Milan.[1–3]

The same authors also determined the structure of these four stereoisomeric polybutadienes, with full data concerning their chain arrangements, as well as the composition of different catalytic systems in which they could be obtained.[4]

In this report new catalysts are described that are highly stereospecific for the synthesis of polybutadiene with an exclusively syndiotactic structure.

Recently other catalytic systems have been reported for the stereoregular polymerization of diolefins. With the aid of catalysts based on cobalt compounds and alkyl aluminum halides,[5] in any Al/Co molar ratio, a polymer with exclusively a 1,4-*cis* structure is obtained from butadiene. Also a polybutadiene of the same type is obtainable with the aid of catalysts prepared from cobalt chloride or bromide and trialkyl aluminum,[6] provided that Al/Co molar ratios lower than 1 are used, and the mixture is allowed to react before its use. In the course of a study concerning the stabilizing effect of the monomer on these catalytic systems,[7] we discovered a new catalyst, by which it is possible to obtain crystalline polymers, whose macromolecules show almost completely the 1,2 enchainment with a syndiotactic structure. These new catalysts[8] consist of Co compounds and an organometallic of the AlR_3 type, as well as mixtures of AlR_3 and AlR_2X, where R is an alkyl radical and X is a halogen.

As Co compounds can be used salts and complexes of Co, inorganic or organic, soluble or insoluble in hydrocarbons. As organometallic component, instead, it is essential to use a trialkyl aluminum. It is not necessary, however, that all of it is trialkyl; mixtures of given ratios of trialkyl aluminum and dialkyl aluminum chloride can be used, so improving both polymerization speed and degree of crystallinity of the polymers.

Any molar ratio between aluminum and transition metal can be used in the catalytic mixture. Practically pure syndiotactic 1,2-polybutadiene has been obtained with Al/Co molar ratios from 0.3 up to 600.

When high aluminum/transition metal ratios are used, the catalytic sys-

tem activity decreases in a short time; in that case, the whole or a major amount of butadiene must be added before adding the alkyl aluminum. Also at low ratios and with cobalt chloride or bromide, it is essential that the catalyst does not become aged before contacting the monomer, otherwise the resulting polymer can contain also macromolecules with a 1,4-*cis* structure. By avoiding the aging, the catalyst, from which 1,4-*cis*-polybutadiene is obtained, is not formed.

Anyhow it is advisable to prepare the catalyst in presence of the monomer, whatever types of metal compounds (VIII group) and aluminum/transition metal ratios are used.

The catalyst formed by the reaction between the transition metal compound and the organometallic compound is apparently soluble.

Insoluble Compounds of Cobalt and AlR_3

The polymerization product obtained with the aid of the catalyst system consisting of an insoluble cobalt compound and AlR_3 is essentially a syndiotactic 1,2-polybutadiene.

The polymer is insoluble in the reaction solvent and appears as very fine and swollen particles suspended in benzene (benzene was used as the solvent in all experiments).

After washing with methanol and drying, the polymer has the appearance of a white and crystalline powder.

In Figure 1 an infrared spectrogram is shown for concerning a crude polybutadiene obtained in this way. It shows all bands that are typical for the vinylic bond R–CH=CH_2, namely these at 908 and 990 cm.$^{-1}$ (CH-bending, out-of-plane), at 1640 cm.$^{-1}$ (C=C stretching), at 1830 cm.$^{-1}$ (vibration harmonic bending, out-of-plane), at 3075 cm and 3090 cm.$^{-1}$ (C–H stretching). The presence of an absorption band at about 660 cm.$^{-1}$ indicates clearly the syndiotactic character of the polymer. The absence of bands typical for the 1,4-*cis* and 1,4-*trans* enchainment helps to show that unsaturation is 100% of the vinylic type.

In Figure 2 is shown an x-ray diffraction diagram for the same sample that was subjected to infrared analysis. It shows all and only the re-

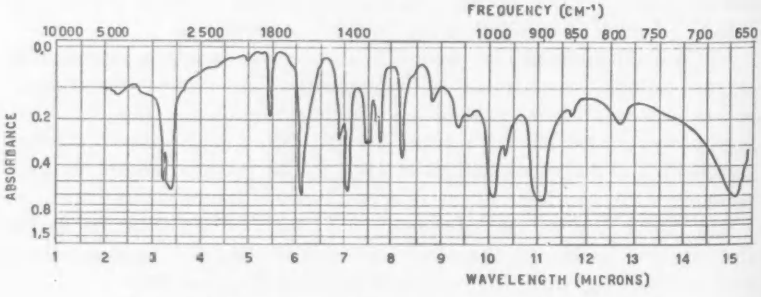


Fig. 1. Infrared spectrum of syndiotactic 1,2-polybutadiene.

TABLE I[a]

Catalyst					X-ray data			Fractionation			
Expt. no.	AlR_3, mmole	Co compound, mmole	Al/Co ratio	Polymer, g.	Crystallinity, %	Structure	Infrared analysis, 1, 2, %	Extracted with acetone, %	Extracted with ether, %	Extracted with benzene, %	Residue, %
1A	$Al(C_2H_5)_3$ 14.3	$CoSO_4$ 42.1	0.34	18.6	75	Syndio	>98	5.5	2	0.5	92
2A	$Al(iC_4H_9)_3$ 14.3	$CoSO_4$ 42.1	0.34	20.5	73	Syndio	>98	6	2.5	0.5	91
3A	$Al(iC_4H_9)_3$ 14.3	$Co_3(PO_4)_2$ 42.1	0.34	15.6	72	Syndio	>98	6	2	1	91
4A	$Al(C_2H_5)_3$ 14.3	Co stearate 42.1	0.34	12	56	Syndio	>98	7	3.5	2	87.5
5A	$Al(C_2H_5)_3$ 14.3	$CoCl_2$ 42.1	0.34	51	75	Syndio	>98	2	1	0.5	96.5
6A	$Al(C_2H_5)_3$ 21	$CoCl_2$ 21	1	43	75	Syndio	—	1.5	1	0.5	97
7A	$Al(C_2H_5)_3$ 33.4	$CoCl_2$ 5	6.67	31	73	Syndio	—	4.5	2	1.8	92.5

[a] Polymerization conditions: benzene 1000 ml.; butadiene 100 g.; temperature 16°C.; time 15 hr.

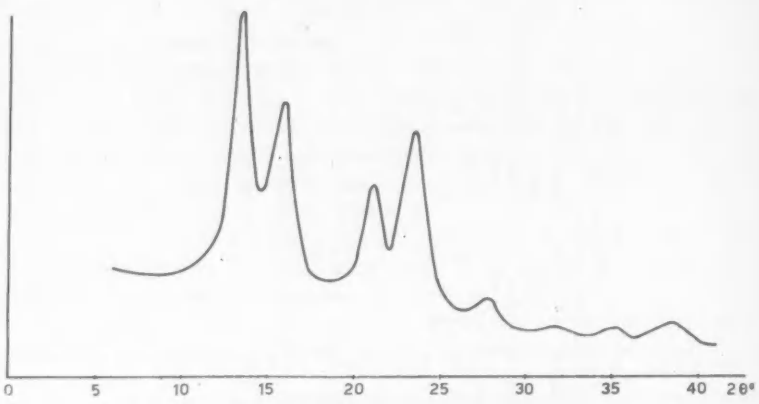


Fig. 2. X-ray diffraction diagram of syndiotactic 1,2-polybutadiene.

flexions of the syndiotactic crystalline 1,2-polybutadiene; the high degree of crystallinity indicates both a regular structure and a good purity of this product.

The same polymer, after repeated extractions with boiling solvents, gave a residue from the benzene extractions (index of syndiotacticity) of 93%.

A number of catalysts obtained from cobalt compounds and aluminum trialkyls were tested. In Table I the results of these experiments are shown. It is apparent that no changes of the stereoisomeric composition are observed on varying the cobalt compound, the trialkyl aluminum and the Al/Co molar ratio in the catalytic system.

Polymerizations 15 hr. in duration were carried out at 16°C., the cobalt compound suspended in the solvent being admitted to the reactor first, then the butadiene, and finally the organometallic compound.

Some polymerizations carried out by adding the butadiene to the system at the same time as the trialkylaluminum (or soon after), gave polymers with the same characteristics, but with a somewhat lower yield (about 10–15%) than those reported in Table I.

Soluble Cobalt Compounds and AlR_3

The use of soluble cobalt compounds simplifies the reaction technology and also allows the reaction to be carried out with very low cobalt concentrations. Also with the aid of these catalysts a polybutadiene with a syndiotactic 1,2 structure is exclusively obtained.

In Table II the results of a number of polymerizations are reported. Also in these tests no changes in the crystallinity and stereoisomeric composition are observed on varying the cobalt compound, the trialkyl aluminum and the Al/Co molar ratio.

Both x-ray crystallinity and syndiotactic index were determined on crude samples, namely on polymers washed with methanol and dried.

TABLE II[a]

Catalyst					X-ray data			Fractionation			
Expt. no.	AlR_3, mmole	Co compound, mmole	Al/Co ratio	Polymer, g.	Crystallinity %	Structure	Infrared analysis, 1, 2, %	Extracted with acetone, %	Extracted with ether, %	Extracted with benzene, %	Residue, %
1B	$Al(C_2H_5)_3$ 33.4	Co stearate·2 Py 16.7	20	8	55	Syndio	—	8.5	3.5	1.5	86.5
2B	$Al(C_2H_5)_3$ 33.4	$CoCl_2$·2 Py 0.187	178	37.6	85.5	Syndio	>98	1	1	0.5	97.5
3B	$Al(C_2H_5)_3$ 33.4	CoI_2·2 Py 0.187	178	38	75	Syndio	>98	1	1	0.5	97.5
4B	$Al(C_2H_5)_3$ 33.4	$CoCl_2$·2P$(C_2H_5)_3$ 0.167	200	25	88.5	Syndio	—	1	1	0.5	97.5
5B	$Al(iC_4H_9)_3$ 33.4	Co stearate·2 Py 0.058	575	21	73	Syndio	>98	4	1	1	96
6B	$Al(C_2H_5)_3$ 33.4	Co stearate·2 Py 0.058	575	38	76	Syndio	>98	1	1	0.50	97.5
7B	$Al(C_2H_5)_3$ 33.4	Co acetylacetonate 0.058	575	14	73.5	Syndio	>98	7	3	0.5	89.5
8B	$Al(C_2H_5)_3$ 37	$CoCl_2$·2Py 0.0615	600	31	76.5	Syndio	>98	1	1	0.5	97.5

[a] Polymerization conditions: benzene 1000 ml.; butadiene 100 g.; temperature 16°C.; time 15 hr.

The polymerization conditions of these runs are the same as previously used with the insoluble cobalt compounds.

The course of the polymerization was observed as a function of time, runs of different duration being carried out with the catalytic system $Al(C_2H_5)_3/CoCl_2 \cdot 2C_5H_5N$ in the molar ratio 430 (1000 ml. benzene; 100 g. "rubber grade" butadiene; temperature 16°C.).

The obtained conversion yields, (Fig. 3) show that, after a rather quick start, the polymerization rate decreases and approaches to zero, when only 40–45% of the butadiene has been converted to polymer.

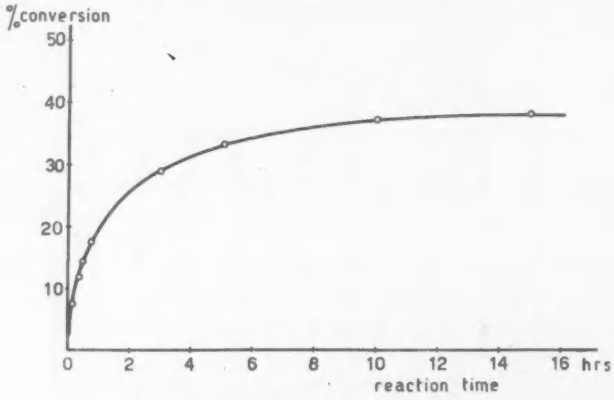
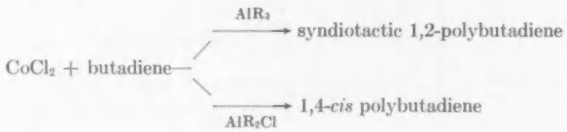


Fig. 3. Conversion vs. reaction time.

Soluble Cobalt Compounds and $AlR_2Cl + AlR_3$ Mixtures

Catalysts made from cobalt compounds and $AlR_2Cl + AlR_3$ mixtures were tested with the purpose of verifying which of them would govern polymerization in presence of both of them; used separately they give, with the same steric purity, a 1,4-*cis*- or syndiotactic 1,2-polybutadiene.



The results of a number of polymerizations carried out with the aid of the system consisting of $CoCl_2.2C_5H_5N$ and several $Al(C_2H_5)_2Cl + Al(C_2H_5)_3$ mixtures are reported in Table III.

By operating with a content of $Al(C_2H_5)_2Cl$ in the mixture of between 12–50 mole-%, a syndiotactic polybutadiene is obtained with a faster reaction. The degree of crystallinity of the polymers is also increased with respect to the one where only $Al(C_2H_5)_3$ was used in the catalytic system.

TABLE III[a]

Expt. no.	Alkyl aluminum: $Al(C_2H_5)_3$, mmole	Alkyl aluminum: $Al(C_2H_5)_2Cl$, mmole	Al/Co ratio	Polymer, g.	Infrared analysis: 1,4-*trans*, %	Infrared analysis: 1,4-*cis*, %	Infrared analysis: 1, 2, %	X-ray crystallinity, %	Structure
1C	33.4	—	430	20.5	—	—	>98	77	Syndio
2C	29.3	4.1	430	29.1	—	—	>98	79	Syndio
3C	25	8.4	430	31.3	—	—	>98	83	Syndio
4C	18.3	15.1	430	35	—	—	>98	87.5	Syndio
5C	16.7	16.7	430	36.4	—	—	>98	91	Syndio
6C	15.8	17.6	430	30.4	—	—	>98	90	Syndio
7C	15.3	18.1	430	10.4	—	—	>98	71	Syndio
8C	13.1	20.3	430	34.1	6.2	81	12.8	Amorphous	—
9C	11.6	21.8	430	55.2	5.1	86	8.1	Amorphous	—
10C	8.3	25.1	430	79	3.2	90	6.8	Amorphous	—
11C	5	28.4	430	88	2.1	95	2.9	Amorphous	—
12C	—	33.4	430	98	2.1	96	1.9	Amorphous	—

[a] Polymerization conditions: $CoCl_2.2C_5H_5N$ 0.077 mmole; benzene 1000 ml.; butadiene 100 g.; temperature 16°C.; time 1 hr.

By further increasing the amount of the diethylaluminum chloride, the activity decreases quickly and becomes about zero, when the percentage becomes 55; beyond this limit, a progressive change of the catalyst stereospecificity is observed, so that the polymer contains increasing amounts of chains with a 1,4-*cis* structure, with increasing $Al(C_2H_5)_2Cl$ content.

Similar results, reported in Table IV, are obtained by using mixtures in the established ratios of $Al(i\text{-}C_4H_9)_3$–$Al(i\text{-}C_4H_9)_2Cl$; $Al(C_2H_5)_3$–$Al(i\text{-}C_4H_9)_2Cl$; $Al(i\text{-}C_4H_9)_3$–$Al(C_2H_5)_2Cl$.

The increase of the catalytic activity is apparent in experiment 3D; the amount of polymer obtained under otherwise similar conditions is 6.5 times as large as that in the reference run without $Al(C_2H_5)_2Cl$.

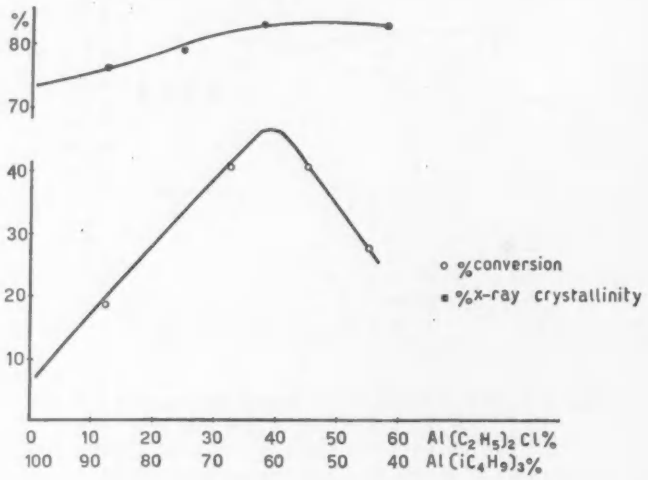


Fig. 4. Conversion and x-ray crystallinity vs. content of $Al(C_2H_5)_2Cl$.

In Figure 4 are shown plots of the conversion and crystallinity a function of the amount of monohalide in the mixture $Al(i\text{-}C_4H_9)_3$–$Al(C_2H_5)_2Cl$. The results are limited to the range of syndiotactic 1,2-polybutadiene.

From what has been said above, it is apparent that the catalytic system consisting of AlR_3 or AlR_3–AlR_2Cl mixtures with a molar ratio higher than 1, and cobalt compounds, will direct the butadiene polymerisation only towards the syndiotactic 1,2 structure.

So far these catalysts have been studied only in connection with the stereoisomeric composition of the obtained polymers. The results so achieved, however, have brought out a feature of these catalytic cobalt complexes: their different and considerable stereospecificity depends upon the organoaluminum compound used.

TABLE IV[a]

Expt. no.	Alkyl aluminum: $AlCR_3$, mmole		Alkyl aluminum: AlR_2Cl, mmole		Al/Co ratio	Polymer, g.	Infrared analysis: 1,4-*trans*, %	Infrared analysis: 1,4-*cis*, %	Infrared analysis: 1,2, %	RX crystallinity, %	Structure
1D	$Al(i\text{-}C_4H_9)_3$	33.4	—		430	7.2	—	—	>98	75	Syndio
2D	$Al(i\text{-}C_4H_9)_3$	16.7	$Al(i\text{-}C_4H_9)_2Cl$	16.7	430	39.5	—	—	>98	80	Syndio
3D	$Al(i\text{-}C_4H_9)_3$	20.9	$Al(C_2H_5)_2Cl$	12.5	430	47.5	—	—	>98	84	Syndio
4D	$Al(C_2H_5)_3$	18.3	$Al(i\text{-}C_4H_9)_2Cl$	15.1	430	28.2	—	—	>98	79	Syndio
5D	$Al(i\text{-}C_4H_9)_3$	16.7	$Al(C_2H_5)_2Cl$	16.7	430	34	—	—	>98	84	Syndio
6D	$Al(i\text{-}C_4H_9)_3$	18.3	$Al(C_2H_5)_2Cl$	15.1	430	41	—	—	>98	84	Syndio

[a] Polymerization conditions: $CoCl_2 \cdot 2C_5H_5N$ 0.077 mmole; benzene 1000 ml.; butadiene 100 g.; temperature 16°C.; time 1 hr.

Experimental

Equipment. Polymerizations were carried out in a stainless steel autoclave of 2000 ml. capacity, fitted with an anchor-type stirrer and an outer jacket for circulating a thermostatic liquid.

Liquid reagents were charged into the reactor by suction, after removing air and moisture by repeated evacuations and filling with dry nitrogen.

Butadiene was transferred into the autoclave from a small bottle, where it had been previously weighed.

At the end of the polymerization the catalyst was inactivated by 50 ml. CH_3OH. The polymer was washed with methanol, was collected by filtration, and then vacuum dried at 50°C. These operations were carried out in absence of air, (in an inert gas atmosphere).

Reagents. All polymerizations were carried out using as solvent a pure grade Carlo Erba benzene dried on activated SiO_2.

The butadiene was a Phillips "rubber grade" product, previously distilled in order to remove any stabilizing agent.

Aluminumalkyls were Montecatini products.

Cobalt salts and compounds were pure grade Carlo Erba products; some of them were prepared according to the literature methods.[5]

Analytical Tests. The infrared analyses[2] were carried out on solid samples, in form of sheets, obtained by cold compression.

For the x-rays examinations, a diffractometer fitted with a Geiger counter was used. The per cent crystallinity was determined by separating in the spectrogram the amorphous phase from the crystalline one according to the method employed for polypropylene.[9]

The solvent extractions were made with the use of hot extractors according to known techniques.[3]

We wish to express our very warm appreciation to Dr. C. A. Ceselli and Mr. Camia for their infrared analyses, as well as to Dr. G. Lanzavecchia for valuable x-ray examinations.

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Synopsis

The stereospecific polymerization of butadiene with catalyst containing a trialkylaluminum or a mixture of trialkylaluminum and a dialkylhalogenaluminium, and mixtures and derivatives of cobalt and other metals of group VIII has been described. By these methods syndiotactic 1,2-polybutadienes can be obtained, with a high degree of cristallinity and purity of steric structure. With the same catalytic systems (e.g., trialkylaluminium and cobalt chloride or derivatives) highly pure 1,4-*cis*-polybutadienes can be prepared. The reaction conditions directing the polymerization in one or in the other stereoisomeric polymer have been compared. Results of x-ray analysis and infrared spectrometry are reported. These experiments confirm the exceptional selectivity of cobalt catalysts, with which several stereoisomeric polymers of butadiene can be obtained.

Résumé

La polymérisation stéréospécifique du butadiène est décrite à l'aide de catalyseurs dérivant d'un aluminium tri-alcoyle ou bien de mélanges d'un aluminium tri-alcoyle et d'un aluminium di-alcoyle mono-halogénure, et de plusieurs ensembles et composés de cobalt et d'autres métaux du VIII groupe. Moyennant ces catalyseurs on peut obtenir des poly-butadiènes avec structure 1,2-syndiotactique, caractérisés par une cristallinité et par une pureté stérique trés élevées. Au moyen de ces mêmes systèmes catalytiques (par exemple ceux constitués d'aluminium tri-alcoyle et de chlorure de cobalt ou de ses ensembles) on peut aussi préparer du poly-butadiène 1,4-*cis* d'une même pureté stérique élevée; on compare les conditions de réaction qui permettent de diriger la polymérisation vers l'une ou l'autre des deux formes stéréoisomères. On rapporte les résultats des examens aux rayons X et spectroscopiques (I.R.) des polymères obtenus. Les expériences décrites confirment l'éclecticité des catalyseurs au cobalt, à l'aide desquels on peut obtenir plusieurs polymères stéréoisomères du butadiène.

Zusammenfassung

Die stereospezifische Polymerisation von Butadien mit Katalysatoren, die sich von einem Trialkylaluminium oder von Mischungen eines Trialkylaluminiums mit einem Dialkylaluminiummonohalogenid ableiten, und mehreren Systemen mit Cobaltverbindungen und Verbindungen anderer Metalle der VIII Gruppe wird beschrieben. Mittels dieser Katalysatoren können Polybutadiene mit 1,2-syndiotaktischer Struktur und sehr hoher Kristallinität und sterischer Reinheit erhalten werden. Mit den gleichen Katalysatorsystemen (z.B. den aus Trialkylaluminium und Kobaltchlorid bestehenden) kann man auch 1,4-*cis*-Polybutadien von gleich hoher sterischer Reinheit darstellen; die

Reaktionsbedingungen, die zur Bildung der einen oder anderen der beiden stereoisomeren Formen führen, werden verglichen. Die Ergebnisse der Röntgen- und IR-Untersuchung der erhaltenen Polymeren werden mitgeteilt. Die beschriebenen Versuche bestätigen die Selektivität der Kobaltkatalysatoren, mit deren Hilfe man mehrere stereoisomere Butadienpolymere erhalten kann.

Discussion

G. Smets (*Louvain, Belgique*): Is there an important reduction of the cobalt salt during the initiation and polymerization, and has one some ideas concerning the nature of organocobalt compound which is formed by interchange?

E. Susa: The triethylaluminum, in absence of monomer, reduces Co^{++} to metallic cobalt with gas evolution. The reaction is slowed down in presence of monomer, but it is not stopped. The reduction also takes place during initiation and polymerization; actually we found metallic cobalt in the polymer. This reduction probably occurs through the formation of an organocobalt compound, but at the moment we are not able to give information about its nature.

Y. Y. Tan (*Delft, Hollande*): In view of the high reactivity of double bonds in the side chains of 1,2-syndiotactic polybutadienes, is there no chance of the formation of insoluble products due to crosslinking and/or products with longer side chains due to branching?

(Since the answer was: they were all insoluble, the question is: was the insolubility due to high crystallinity of the products or due to their partial crosslinking.)

E. Susa: During the whole polymerization the polymer always remains insoluble. The x-rays crystallinity is very high, therefore the number of crosslinking present should be very low or inexistent and the polymer insolubility is due to the crystallinity.

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Polymérisation du Propylène à Polymère Syndiotactique

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I. INTRODUCTION

Les premiers résultats concernant la polymérisation du propylène à polymère syndiotactique[1] avaient montré que ce type de polymérisation se différencie nettement de la polymérisation à polymère isotactique. En effet, tandis que dans ce dernier cas la présence d'un substrat cristallin dans le système catalytique semble nécessaire (ou du moins très utile) pour l'obtention d'un polymère cristallin, cela n'est pas le cas de la polymérisation à polymère syndiotactique, étant donné qu'ici le système catalytique peut être homogène (du moins apparemment).

Avec des systèmes catalytiques particuliers (hétérogènes et à base de composés de titane),[2,3] le polypropylène syndiotactique peut être obtenu à des températures assez élevées (même >70°C), mais avec les systèmes catalytiques homogènes que nous avons davantage étudiés (à base de composés de vanadium), le polypropylène syndiotactique s'obtient seulement si l'on opère à des températures suffisamment basses (par ex. −70°C).

Il est bien connu que même dans le cas de plusieurs monomères vinyliques non hydrocarbures,[4–8] le polymère syndiotactique peut être obtenu par mécanisme de polymérisation radicalaire surtout si la température de polymérisation est très basse. La régularité stérique que l'on a dans ces cas serait due au fait que l'enchaînement syndiotactique, lors de la croissance d'une chaîne polymérique dont l'extrémité est libre (par exemple constituée par un radical), est favorisé par rapport à celui isotactique.[9–11] (Huggins[12] avait déjà prévu en 1944 que la régularité stérique des polymères obtenus par polymérisation radicalaire doit augmenter lorsque la température de polymérisation diminue.)

D'autres auteurs[13] ont calculé que même dans le cas du propylène, pour des mécanismes soit radicalaires, soit purement cationiques, la polymérisation à polymère syndiotactique devrait être favorisée, pourvu que l'approche du monomère au groupe terminal de la chaîne en croissance ait lieu d'une façon déterminée.

Dans ce travail nous reportons les résultats plus récents que nous avons obtenus dans l'étude de la polymérisation du propylène à polymère syndiotactique, avec des systèmes catalytiques qui sont apparemment homogènes;

ces résultats ne sont pas encore suffisants pour déduire d'une façon univoque un mécanisme complet, mais leur interprétation nous a conduit à la conclusion que dans notre cas la polymérisation doit être stéréospécifique et que le mécanisme peut être retenu du type anionique coordiné.

II. RÉSULTATS OBTENUS

A. Essais de Polymérisation

Les systèmes catalytiques dont nous parlons en détail dans cette communication sont préparés à partir de VCl_4 et d'un composé du type AlR_2X (R = alcoyle; X = halogène) en présence d'une base de Lewis; nous

TABLEAU I
Influence de la Température de Polymérisation[a]

Température de polymérisation, °C	Durée de la polymérisation, h	Polymère obtenu		
		g	$[\eta]$ 100 cm³/g	Index de cristallinité du polymère syndiotactique[b]
−78	24	1,0	1,06	1,65
−57	24	8,45	1,15	0,55
−50	24	13,6	1,08	0,4
−40	24	21,2	1,05	—
+20	24	Traces	—	—
−55	1/2	0,2	0,44	1,1
−40	1/4	0,35	0,38	1,25

[a] Conditions de polymérisation: toluène: 100 cm³; VCl_4: 1×10^{-3} moles; anisole: 1×10^{-3} moles; $Al(i\text{-}C_4H_9)_2Cl$: 5×10^{-3} moles; propylène: 80 g; introduits dans l'ordre; température de préparation du catalyseur: −78°C.

[b] L'index de cristallinité est défini dans le paragraphe G.

TABLEAU II
Influence dels Durée de la Polymérisation[a]

Durée de la polymérisation, h	AlR_2Cl	Polymère obtenu		
		g	$[\eta]$, 100 cm³/g	Index de cristallinité du polymère syndiotactique[b]
1/2	$Al(CH_3)_2Cl$	2,45	0,28	0,85
24	$Al(CH_3)_2Cl$	11,8	0,89	0,6
3/4	$Al(C_2H_5)_2Cl$	0,2	—	1,55
6	$Al(C_2H_5)_2Cl$	4,6	0,56	1,3
24	$Al(C_2H_5)_2Cl$	8,2	0,89	1,0
12	$Al(i\text{-}C_4H_9)_2Cl$	0,45	0,74	1,85
24	$Al(i\text{-}C_4H_9)_2Cl$	1,0	1,06	1,65

[a] Conditions de polymérisation: toluène: 100 cm³; anisole: 1×10^{-3} moles; VCl_4: 1×10^{-3} moles; AlR_2Cl: 5×10^{-3} moles; propylène: 80 g; introduits dans l'ordre; $t = -78$°C.

[b] Voir Tableau I.

TABLEAU III
Influence de Différents Types de Bases de Lewis[a]

Base de Lewis	Polymère obtenu		
	g	$[\eta]$, 100 cm³/g	Index de cristallinité du polymère syndiotactique[b]
Thiofène	1,1	0,76	0,5
Anisole	1,0	1,06	1,65
Acétate d'éthyle	1,35	0,91	0,65
Furane	1,25	0,71	1,25
Ether éthylique	1,1	1,10	0,95
Cyclohexanone	1,0	1,00	0,9
Pyridine	0	—	—

[a] Conditions de polymérisation: toluène: 100 cm³; base de Lewis: 1×10^{-3} moles; VCl_4: 1×10^{-3} moles; $Al(i\text{-}C_4H_9)_2Cl$: 5×10^{-3} moles; propylène: 80 g; introduits dans l'ordre; $t = -78°C$; durée des polymérisations: 24 h.

[b] Voir Tableau I.

TABLEAU IV
Influence des Rapports Anisole/VCl_4 et Al/Anisole[a]

Anisole VCl_4 (mol)	$Al(i\text{-}C_4H_9)_2Cl$ anisole (mol)	Al/V (mol)	Polymère obtenu		
			g	$[\eta]$, 100 cm³/g	Index de cristallinité du polymère syndiotactique[b]
0	∞	5	1,05	0,66	0,4
0,5	10,0	5	1,15	1,15	0,7
1	5,0	5	1,0	1,06	1,67
2	2,5	5	1,6	1,02	1,5
3	0,6	5	1,2	0,94	1,25
4	0,8	5	0,55	0,86	1,0
5	1,0	5	0	—	—
11	2,27	25	0,6	0,98	0,3

[a] Conditions de polymérisation: toluène: 100 cm³; anisole: variable; $Al(i\text{-}C_4H_9)_2Cl$: variable; propylène: 80 g, introduits dans l'ordre; $t = -78°C$; durée de la polymérisation: 24 h.

[b] Voir Tableau I.

TABLEAU V
Influence du Rapport $Al(i\text{-}C_4H_9)_2Cl/VCl_4$

Al/V (mol)	Polymère obtenu		
	g	$[\eta]$, 100 cm³/g	Index de cristallinité du polymère syndiotactique[b]
4	0,9	0,90	1,7
5	1,0	1,06	1,65
10	3,0	1,50	1,1

[a] Conditions de polymérisation: toluène: 100 cm³; anisole: 1×10^{-3} moles; VCl_4: 1×10^{-3} moles; $Al(i\text{-}C_4H_9)_2Cl$: variable; introduits dans l'ordre; $t = -78°C$; durée de la polymérisation: 24 h.

[b] Voir Tableau I.

TABLEAU VI

Influence de l'Ordre d'Introduction des Réactifs pendant la Préparation du Catalyseur[a]

Ordre d'introduction des réactifs	Pyridine, moles	Al/V (mol)	Polymère obtenu: g	Polymère obtenu: $[\eta]$, 100 cm³/g	Polymère obtenu: Index de cristallinité du polymère syndiotactique[b]
Anisole–VCl_4–$Al(i\text{-}C_4H_9)_2Cl$	0	5	1,1	1,06	1,65
Anisole–$Al(i\text{-}C_4H_9)_2Cl$–VCl_4	0	5	0,9	1,80	0,85
Pyridine–VCl_4–anisole–$Al(i\text{-}C_4H_9)_2Cl$	1×10^{-3}	6	0	—	—
Anisole–VCl_4–$Al(i\text{-}C_4H_9)_2Cl$–pyridine	1×10^{-3}	6	0,9	0,89	0,8

[a] Conditions de polymérisation: toluène: 100 cm³; VCl_4: 1×10^{-3} moles; anisole: 1×10^{-3} moles; $t = -78°C$; durée de la polymérisation: 24 h.

[b] Voir Tableau I.

TABLEAU VII

Influence du type de Composé AlR_2X[a]

AlR_2X	Température de polymérisation, °C	Polymère obtenu: g	Polymère obtenu: $[\eta]$, 100 cm³/g	Polymère obtenu: Index de cristallinité du polymère syndiotactique[b]
$Al(CH_3)_2Cl$	−78	11,8	0,89	0,6
$Al(C_2H_5)_2Cl$	−78	8,2	0,89	1,0
$Al(i\text{-}C_4H_9)_2Cl$	−78	1,0	1,06	1,65
$Al(neo\text{-}C_5H_{11})_2Cl$	−78	2,1	0,67	1,85
$Al(i\text{-}C_4H_9)_2Cl$	−60	8,4	1,15	0,55
Al(méthylstyril)$_2$Cl	−60	4,5	1,20	0,8
$Al(C_2H_5)_2F$	−78	0,4	4,80	0[c]
$Al(C_2H_5)_2Br$	−78	0,4	—	0[c]
$Al(C_2H_5)_2I$[d]	−78	0,2	1,26	0[c]

[a] Conditions de polymérisation: toluène: 100 cm³; anisole: 1×10^{-3} moles; VCl_4: 1×10^{-3} moles; AlR_2X: 5×10^{-3} moles; propylène: 80 g; introduits dans l'ordre; durée des polymérisations 24 h; température de préparation du catalyseur: −78°C.

[b] Voir Tableau I.

[c] Le polymère présente une faible cristallinité due à polypropylène isotactique.

[d] Durée de l'essai: 12 h.

avons étudié en particulier l'influence, sur les résultats de la polymérisation, des facteurs suivants: température de polymérisation (Tableau I), durée de la polymérisation (Tableaux I et II), type de base de Lewis (Tableaux III et VI), rapport base de Lewis/VCl_4 (Tableau IV), rapport Al/V (Tableau V), ordre d'introduction des réactifs pendant la préparation du

TABLEAU VIII

Influence de l'addition de AlR_3 aux systèmes VCl_4–anisole–AlR_2Cl[a]

VCl_4, moles $\times 10^3$	Anisole, moles $\times 10^3$	AlR_2Cl, moles $\times 10^3$	$Al(C_2H_5)_3$, moles $\times 10^3$	Durée de la polymerisation, h	Polymère obtenu: g	$[\eta]$, 100 cm^3/g	Index de cristallinité du polymère syndiotactique[b]
1	3	5[c]	—	24	1,2	0,94	1,5
0,5	1,5	1,5[d]	1	3,5	3,7	5,10	Amorphe
1	3	3[d]	2	24	67	9,00	Amorphe

[a] Conditions de polymérisation: toluène: 100 cm^3; propylène: 80 g; $t = -78°C$.
[b] Voir Tableau I.
[c] $Al(i\text{-}C_4H_9)_2Cl$.
[d] $Al(C_2H_5)_2Cl$; les réactifs ont été introduits dans l'ordre suivant: toluène, anisole, VCl_4, AlR_2Cl et AlR_3 complexé au préalable (selon le rapport 1:1) avec de l'anisole.

catalyseur (Tableau VI), type de composé AlR_2X employé (Tableau VII), et addition de AlR_3 au catalyseur (Tableau VIII).

Enfin nous avons observé le comportement d'un de nos systèmes catalytiques types, dans l'homopolymérisation de l'éthylène et du butène-1 et dans la copolymérisation éthylène-propylène et nous avons effectué aussi des essais de synthèse d'un copolymère à deux blocs éthylène-propylène, en alimentant successivement les deux monomères dans le réacteur.

Nous avons observé que le butène-1 ne homopolymérise pas (par ex. à $t < -50°C$) tandis que l'éthylène homopolymérise rapidement même à basse température; ce monomère copolymérise aussi avec le propylène, pour fournir, selon les conditions, des copolymères "random" ou à hétéroblocs.

Un copolymère à deux séquences éthylène-propylène que nous avons préparé, a été soumis à l'extraction avec des solvants (Tableau IX); l'examen infra-rouge a montré que soit la fraction extraite par le *n*-heptane, soit le résidu, contiennent du polyéthylène et du polypropylène syndiotactique; puisque le polyéthylène obtenu par homopolymérisation, sous

TABLEAU IX

Copolymère Séquencé Éthylène–Propylène

Fraction: Type	Fraction: %	Éthylène dans le polymère, %	Index de cristallinité du polymère syndiotactique[a]
extrait éther	18	—	—[b]
extrait heptane	51	4	1,05[c]
résidu	31	72	—[c]
polymère	brut	18	0,8[c]

[a] Voir Tableau I.
[b] Amorphe.
[c] Le produit montre cristallinité due à polypropylène syndiotactique et à polyéthylène.

les mêmes conditions de polymérisation et avec les mêmes systèmes catalytiques, est insoluble dans le *n*-heptane, tandis que le polypropylène est au contraire complètement soluble dans le *n*-heptane à l'ébullition, on doit conclure que soit l'extrait par le *n*-heptane, soit le résidu du polymère obtenu dans la copolymérisation séquencée, contiennent des chaînes polymériques contenant en même temps une séquence de polyéthylène et une séquence de polypropylène.

B. Examen des Produits de Décomposition des Catalyseurs

Les systèmes catalytiques employés sont apparemment homogènes et stables seulement à basse température (environ $< -40°C$). Lorsqu'on les porte à température ambiante, leur activité catalytique dans la polymérisation du propylène tombe pratiquement à zéro et, après quelque temps, ils donnent lieu à la formation d'un précipité. Dans le cas des catalyseurs que nous avons employés, les précipités contiennent principalement du VCl_2 impur de composés d'aluminium, de bases de Lewis et de groupes alcoyles. Des résultats tout à fait semblables avaient déjà été obtenus dans un travail effectué dans notre Institut concernant l'étude de la réaction du vanadium triacétylacétonate avec l'aluminium diéthyl monochlorure.[14]

Il est intéressant de remarquer que dans le cas des mêmes réactions effectuées avec le $TiCl_4$ ou le titane triacétylacétonate—qui ne fournissent pas avec le AlR_2Cl des catalyseurs pour la polymérisation du propylène à polymère syndiotactique—les précipités contiennent principalement du $TiCl_3$.

C. Examen et Nature des Polymères Obtenus

Les polymères obtenus sont cristallins, comme on peut l'observer d'après le spectre Geiger obtenu aux rayons X (Fig. 1); la comparaison avec le spectre du polypropylène isotactique montre que la cristallinité de ces polymères est due seulement à la présence de produit syndiotactique.

On peut en outre observer que la cristallinité—détectable par l'examen aux rayons X—des polypropylènes syndiotactiques que nous avons obtenus n'est pas très élevée.*

Le spectre infra-rouge des échantillons à l'état solide, montre une bande à 11,53 μ qui est caractéristique du polypropylène syndiotactique.[2]

Les polymères bruts que nous avons préparés ont des viscosités intrinsèques pas très élevées (souvent $\simeq 1$) et ils sont entièrement solubles dans le *n*-heptane à l'ébullition.

A partir de ces polymères bruts il n'a été possible de séparer, ni par extraction avec des solvants, ni par séparation chromatographique,[2] des fractions sensiblement plus riches en polymère syndiotactique, que le polymère original.

* Pour cette raison il serait plus correct de definir "polypropyléne montraut une cristallinité due à la forme syndiotactique" ce que nous avois dénominé "polypropylène syndiotactique."

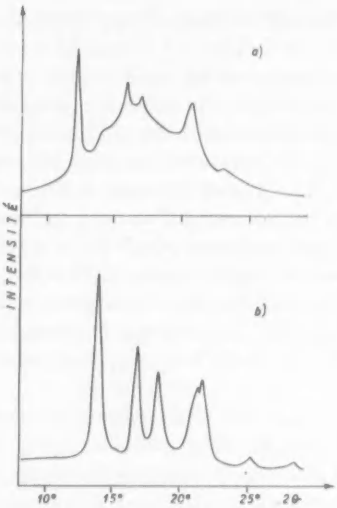

Fig. 1. Spectres Geiger aux rayons X (CuKα) de polypropylènes: (*a*) syndiotactique (produit partiellement cristallin, index de cristallinité du polymère syndiotactique = 1,7) (*b*) isotactique (produit très cristallin).

Cela démontre que toutes les chaînes polymériques ont une composition stérique pratiquement homogène; ce résultat est en accord avec l'apparente homogénéité du système catalytique. On doit donc admettre que chaque macromolécule—étant donnée la faible cristallinité du polymère—est à stéréoblocs, c'est à dire contenant des séquences syndiotactiques alternées à des séquences ayant une configuration stérique différente.

III. DISCUSSION DES RÉSULTATS

A. Type de Mécanisme

Il est intéressant de discuter le mécanisme de la polymérisation du propylène à polymère syndiotactique, en tenant compte du fait que les polymères syndiotactiques de plusieurs monomères vinyliques non hydrocarbures peuvent être obtenus à basse températures par mécanisme radicalaire;[4–6] en outre il est connu que certains catalyseurs du type Ziegler fournissent des radicaux qui, dans certains cas, peuvent initier des polymérisations (par ex. du chlorure de vinyle[7]) en donnant lieu à des polymères syndiotactiques.

Dans le cas de la synthèse du polypropylène syndiotactique que nous avons étudié, nous pensons toutefois de pouvoir exclure le mécanisme radicalaire, pour les raisons suivantes:

1. La régularité stérique des polymères que nous avons obtenus dépend: (*a*) des rapports anisole/VCl_4 ou $Al(i\text{-}C_4H_9)_2Cl$/anisole, même pour des

polymères qui ont été préparés à la même température et qui ont a peu près la même masse moléculaire (Tableau IV); (*b*) du rapport Al/V (Tableau V); dans le cas des systèmes à base de VAc_3 (ou Ac = résidue acétyl acétonique),[1] seulement les systèmes catalytiques préparés avec certains rapports Al/V, fournissent des polymères syndiotactiques; pour d'autres rapports Al/V le polymère que l'on obtient est complètement amorphe aux rayons X;[1] (*c*) des dimensions des groupes alcoyles liés au composé d'aluminium utilisé pour préparer le système catalytique (si l'on compare les essais ayant la même durée de polymérisation) (Tableau VII); (*d*) des différentes bases de Lewis (Tableaux III et IV).

2. Le polypropylène syndiotactique peut être obtenu à des températures allant au moins jusqu'à 80°C pourvu que l'on emploie des systèmes catalytiques à base de composés de titane et d'aluminiums alcoyles[2] ou de sodium alcoyle.[3]

3. Malgré que le VCl_4 puisse être réduit par des composés autres que AlR_2Cl, comme par exemple AlR_2F, AlR_2Br, AlR_2I, LiR, ZnR_2 seulement les systèmes à base de AlR_2Cl fournissent du polymère syndiotactique (Tableau VII).

Si la formation du polypropylène syndiotactique à basse température était due seulement à des facteurs énergétiques concernant la stabilité relative des différents types de configuration stérique des motifs monomères à l'extrémité libre de la chaîne en croissance, et si dans notre cas le mécanisme de la polymérisation était radicalaire, les polymères ayant la même masse moléculaire, obtenus à la même température de polymérisation, devraient avoir tous la même régularité stérique; c'est ce que l'on observe dans le cas des monomères vinyliques non hydrocarbures (par ex. chlorure de vinyle), lorsqu'ils polymérisent par mécanisme radicalaire, en fournissant des polymères syndiotactiques.[7]

En ce qui concerne les calculs de Fordham[9] (qui ont été effectués pour le chlorure de vinyle), nous pensons que leur application au cas du propylène ne montrerait pas que dans ce dernier cas l'enchaînement syndiotactique à l'extrémité libre d'une chaîne de polypropylène en croissance est sensiblement plus favorisé que l'enchaînement isotactique.

En effet la différence entre les énergies d'activation des processus de propagation qui devraient fournir respectivement l'enchaînement isotactique et l'enchaînement syndiotactique, dépend soit des facteurs stériques soit des facteurs électroniques concernant la nature du substituant dans le monomère vinylique; les calculs et les données expérimentales relatifs au chlorure de vinyle[9] et aux vinyl esters[6] montrent que les facteurs électroniques sont beaucoup plus importants que les facteurs stériques; à ce sujet, dans le cas du propylène, la composante électronique est pratiquement nulle et la composante stérique ne semble pas suffisamment importante pour favoriser, d'une façon marquée, l'enchaînement syndiotactique. Ces observations semblent confirmées par le fait que dans le cas du chlorure de vinyle la différence entre les énergies d'activation des deux types d'enchainement est égale à environ seulement 500 cal/mol;[5] il est vraisem-

blable que dans le cas du propylène cette différence soit beaucoup plus petite.*

Nous pensons aussi de pouvoir exclure un mécanisme purement cationique. En effet, dans ce cas, il serait assez difficile d'expliquer le fait que les systèmes catalytiques que nous avons employés homopolymérisent rapidement l'éthylène en fournissant des hauts polymères linéaires et qu'ils ne homopolymérisent pas le butène-1. En outre la formation de copolymères à blocs éthylène–propylène (Tableau IX) montre que l'éthylène peut effectivement polymériser sur les mêmes centres de polymérisation qui fournissent le polypropylène syndiotactique.

D'autres essais effectuées avec de l'aluminium alcoyle contenant du ^{14}C,[17] ont montré que les chaînes polymériques de polypropylène, contiennent les groupes alcoyliques provenant de l'aluminium alcoyle utilisé pour préparer le catalyseur. Même ce résultat peut être difficilement interprété sur la base d'un mécanisme cationique.

Ces observations nous ont conduit à la conclusion que dans notre cas le mécanisme de polymérisation est encore du type anionique coordiné, comme dans le cas de la polymérisation du propylène à polymère isotactique. (Il convient de rappeler que nous entendons par polymérisations anioniques coordinées des monomères vinyliques hydrocarbures, les polymérisations dans lesquelles le stade de propagation des chaînes polymériques est précédé par une complexation du monomère sur un métal faisant partie du complexe catalytique, l'addition du motif monomère ayant ensuite lieu par insertion sur une liaison métal-carbone, l'atome de carbone de cette liaison ayant une charge partiale négative.)

B. Complexes Catalytiques

Les systèmes catalytiques stéréospécifiques dans la polymérisation du propylène à polymère syndiotactique, que nous avons étudiés, peuvent être préparés à partir de composés de vanadium soit tétravalents (VCl_4) soit trivalents (VAc_3).[1] Dans les deux cas, les produits de la décomposition thermique des systèmes catalytiques contiennent le vanadium à l'état bivalent, sous forme de VCl_2. Nous pensons que dans notre cas les complexes catalytiques contiennent le vanadium à l'état trivalent, sous forme de VCl_2R.† Ce composé se forme comme produit intermédiaire soit pendant la réduction de VCl_4 à VCl_2 sous l'action des composés organom-

* Quant aux calculs de Ferstandig et de Goodrich[13] selon lesquels un mécanisme radicalaire, ou cationique, du propylène devrait forunir à basse température des polymères syndiotactiques, nous observerons qu'ils ne sont confirmés par aucun fait expérimental; au contraire, la polymérisation du propylène effectuée par Fontana[15] à basse température par mécanisme cationique, fournit un polymère amorphe; ce polymère ne présente, ni aux rayons X, ni aux rayons IR, cristallinité du type syndiotactique.[16]

† Les systèmes préparés à basse température à partir de VCl_3 cristallin et de AlR_2Cl sont eux aussi inactifs dans la polymérisation du propylène à polymère syndiotactique. Cela peut être du au fait, qu'à basse température, à cause de l'énergie réticulaire du VCl_3, la réaction d'alcoylation de ce composé n'a pas lieu.

étalliques, soit pendant la chloruration et la successive réduction du VAc_3 sous l'action de $Al(C_2H_5)_2Cl$.

Ces hypothèses concordent avec les résultats obtenus dans notre Institut, et reportés dans une publication précédente,[14] concernant la polymérisation du butadiène, à polymère 1,4-*trans*, avec des catalyseurs obtenus à partir de VAc_3 et de $Al(C_2H_5)_2Cl$.

Le VCl_2R n'est pas toutefois la seule composante déterminante des systèmes catalytiques pour la polymérisation du propylène à polymère syndiotactique. En effet la réduction du VCl_4 peut être effectuée avec des composés autres que AlR_2Cl, comme par exemple AlR_2F, AlR_2Br, AlR_2I, LiR, ZnR_2; mais dans aucun de ces cas nous avons obtenu des systèmes catalytiques aptes à polymériser le propylène syndiotactique (Tableau VII).

Ces résultats nous font retenir que, dans le cas des systèmes préparés à partir de VCl_4, le $AlRCl_2$ est une autre composante nécessaire du système catalytique.

Ce composé se forme lors de la réaction:

$$VCl_4 + 2AlR_2Cl \rightarrow VCl_2R + 2AlRCl_2 + R\cdot$$

Cette hypothèse, concernant la présence de $AlRCl_2$ dans les complexes catalytiques stéréospécifiques, est en accord avec le fait que l'addition de AlR_3 ou de AlR_2Cl (au-dessus du rapport Al/V optimum) aux systèmes catalytiques, fait disparaître (Tableau VIII), ou diminuer (Tableau V) la stéréospécificité des systèmes, tandis que leur activité augmente.

En ce qui concerne la conformation des complexes catalytiques stéréospécifiques, les données que nous avons obtenues ne sont pas suffisantes pour avancer des hypothèses assez satisfaisantes. Nous pensons qu'ils soient des produits d'association entre VCl_2R et $AlCl_2R$ où les atomes de métal sont liés entr'eux par des ponts d'halogène. (Récemment il a été trouvé un système catalytique qui serait constitué par $TiCl_3R$ et $AlCl_2R$;[18] ce système, qui est assez semblable à celui que nous décrivons, polymérise l'éthylène à basse température en fournissant des oligopolymères.) La croissance des chaînes polymériques aurait lieu par insertion des unités monomériques sur une des liaisons métal-carbone du complexe, l'atome de carbone ayant une charge partiale négative. Les complexes du type susmentionné sont suffisamment stables si ces ponts sont symétriques. Notre hypothèse est appuyée par le fait que les systèmes préparés à partir de VCl_4 et de AlR_2X sont actifs dans la polymérisation à polymère syndiotactique seulement si X = Cl (Tableau VII); dans ce cas le système est homogène. Si X = F, Br ou I, il se forme un précipité qui polymérise encore le propylène, mais pour fournir un produit qui présente une faible cristallinité seulement de type isotactique.

Plusieurs hypothèses peuvent justifier soit la formation des chaînes polymériques à stéréoblocs, soit la dépendence de la régularité stérique du polymère obtenu de sa masse moléculaire (Tableau II), du rapport Al/V (Tableau V) et de la dimension des groupes alcoyles (Tableau VII). Par

exemple il suffit d'admettre que les systèmes catalytiques contiennent au moins deux espèces de complexes catalytiques, entr'elles à l'équilibre et que seulement une soit stéréospécifique. Cet équilibre pourrait être influencé soit par le rapport Al/V, soit par la dimension des alcoyles provenant du composé d'aluminium utilisé pour préparer le catalyseur, soit par la longueur des chaînes polymériques en croissance, liées aux complexes.

En ce qui concerne l'influence des bases de Lewis, on peut constater que le comportement du système catalytique (en ce qui concerne soit l'activité, soit la stéréospécificité) dépend de leur force (Tableau III). Elles peuvent influencer soit la réaction de formation du catalyseur, soit l'éventuel équilibre dont nous avons parlé ci-dessus. Les bases fortes, comme par exemple la pyridine, empêchent la formation du catalyseur, mais elles n'empêchent pas la polymérisation si le catalyseur a été préparé, au préalable, avec une base faible (Tableau VI); dans ce dernier cas on observe seulement une diminution de la stéréospécificité.

On peut observer aussi que si l'anisole est ajouté au produit de réaction du VCl_4 avec le AlR_2Cl, on obtient un système catalytique moins stéréospécifique que celui obtenu en ajoutant AlR_2Cl au VCl_4 complexé au préalable avec l'anisole (Tableau VI).

D'après ces résultats nous ne pouvons toutefois pas exclure que les bases de Lewis puissent faire partie intégrante des complexes catalytiques.

Pour conclure, nous observerons que le polypropylène syndiotactique est le premier exemple de polymère d'une oléfine ayant telle structure qui ait été préparé. Auparavant on connaissait seulement un autre polymère syndiotactique hydrocarburé: le polybutadiène 1,2 syndiotactique;[19] il est intéressant de remarquer que même dans ce cas les systèmes catalytiques utilisés sont homogènes et qu'ils sont préparés à partir d'un composé d'un métal de transition et d'un composé organométallique de l'aluminium; leur température d'emploi est relativement élevée (>0°C) par rapport à notre cas, leur stéréospécificité dépend du rapport Al/métal de transition et le mécanisme de polymérisation est encore du type anionique coordiné.[19]

IV. PARTIE EXPÉRIMENTALE

A. Réactifs et Solvants

Monomères. Le propylène que nous avons employé contenait plus que 98% de propylène, le reste étant pratiquement du propane. L'éthylène avait un titre >99% le reste étant éthane.

Solvant. Le toluene (produit ERBA RP) après avoir été traité avec H_2SO_4 a été maintenu à l'ébullition pendant 24 heures sur un alliage Na–K. Successivement il était distillé et conservé sous azote.

Vanadium Tétrachlorure. Ce produit nous a été fourni par la Società Montecatini; nous l'avons employé après l'avoir distillé sous vide.

Autres Composés. Anisole, furanne, cyclohexanone, acétate d'éthyle, thiofène, éther diéthylique et pyridine ont été utilisés purs que l'on trouve dans le commerce.

Composés Organométalliques. Les composés ayant la formule générale $AlRCl_2$ et $AlRCl_2$ ont été préparés à partir des aluminiums trialcoyles correspondant par réaction avec le $AlCl_3$ (employé en quantité stoechiométrique), suivie d'une distillation sous vide.

L'aluminium triéthyle et l'aluminium triisobutyle que nous avons utilisés avaient un titre >80% en AlR_3.*

L'aluminium triméthyle a été préparé par déhalogénation (avec du potassium métallique) du sesquiiodure d'aluminium triméthyle. Ce dernier était obtenu à son tour par synthèse directe à partir de l'aluminium métallique et du iodure de méthyle.

Les autres composés ont été préparés selon les méthodes décrites dans a littéraure: aluminium trinéopentyle,[20] aluminium tri-α-méthylstyrile,[21] aluminium tribenzile,[21] aluminium diéthylmonofluorure, monobromure et monoiodure.[22]

B. Essais de Polymérisation

Reproductibilité. Les résultats obtenus dans les essais de polymérisation en ce qui concerne la quantité de polymère obtenu et sa régularité stérique, dépendent sensiblement du degré de pureté du solvant employé.

TABLEAU X
Influence de la Pureté du Solvant[a]

Solvant	Polymère obtenu		
	g	$[\eta]$, 100 cm³/g	Index de cristallinité du polymère syndiotactique[b]
Toluène 99,4%[c]	4,6	0,56	1,3
Toluène 99,6%[d]	2,5	0,41	1,8
Toluène 100%[e]	2,5	0,45	1,8

[a] Conditions de polymérisation: toluene: 100 cm³; anisole: 1×10^{-3} moles; VCl_4: 1×10^{-3} moles; $Al(C_2H_5)_2Cl$: 5×10^{-3} moles; propylène: 80 g; introduits dans l'ordre; $t = -78°C$; durée des polymérisation: 6 h.

[b] Voir Tableau I.

[c] 0,6% d'impuretés constituées par des hydrocarbures C_7 et C_8 et par des traces de thiocomposés.

[d] 0,4% d'impuretés constituéss seulement par des hydrocarbures C_7 et C_8.

[e] Chromatographiquement pur.

Nous avons récemment observé en particulier, que l'emploi de toluène chromatographiquement pur comme solvant permet d'obtenir des polymères ayant une régularité stérique supérieure à celle des produits obtenus

* Ils nous été fournis par la Soc. Montécatini.

en présence de toluène contenant des traces de thiocomposés comme impureté (Tableau X).

Ces résultats peuvent être facilement expliqués si l'on tient compte de l'influence des bases de Lewis sur le comportement des systèmes catalytiques que nous avons étudiés (Tableaux III et VI).

Etant donné que le toluène que nous avons employé dans les différents essais que nous avons effectués, n'était pas toujours chromatographiquement pur, et étant donné. Que l'influence sur le polymérization des impunetés de l'aluminium alcoyle ne peut pos être à pirori negligée, la reproductibilité des résultats que nous avons reportés n'est pas parfaite.

Homopolymérisation du Propylène. Nous décrivons à titre d'exemple un essai de homopolymérisation pour l'obtention du polypropylène syndiotactique. Dans un réacteur de 250 cm³ on introduit, sous azote, 100 cm³ de toluène anhydré. Après avoir refroidi le réacteur à −78°C, à l'aide d'un bain de méthanol et de CO_2 solide, on y introduit successivement 1×10^{-3} moles de anisole, 1×10^{-3} moles de VCl_4 et 5×10^{-3} moles de $Al(i\text{-}C_4H_9)_2Cl$. On ajoute enfin 80 g de propylène. Le réacteur ainsi chargé est maintenu par la suite pendant 24 h à −78°C, sans agitation. Après ce temps le contenu du réacteur (qui a une consistance sirupeuse et une couleur violacée) est coagulé avec un eccès de méthanol, en présence d'une petite quantité d'acide chlorydrique.

Le polymère ainsi précipité est par la suite filtré et lavé plusieurs fois, avec du méthanol pur, et enfin séché sous vide à 60°C. On obtient 1 g de produit ayant viscosité intrinsèque égale à 1,1 (100 cm³/g), dont le spectre Geiger aux rayons X montre les pics caractéristiques du polypropylene syndiotactique.

Copolymère à Deux Blocs Éthylène–Propylène. Dans un réacteur ayant une capacité de 250 cm³, maintenu sous azote à −78°C, on introduit, dans l'ordre suivant: 100 cm³ de toluène anhydre; 1×10^{-3} moles de anisole; 1×10^{-3} moles de VCl_4 et 5×10^{-3} moles de $Al(i\text{-}C_4H_9)_2Cl$. On ajoute ensuite lentement, pendant 20 min, environ 4000 N cm³ d'éthylène marqué avec ^{14}C. On fait passer ensuite dans la solution, de l'azote pur, pendant 20 min. Après cette opération, on ajoute, dans le réacteur ne contenant plus d'éthylène, 80 g de propylène. Après 24 h on obtient 5,4 g de polymère contenant 18% en poids d'éthylène.

Une partie de ce polymère est fractionnée par extraction avec l'éther éthylique et successivement avec le *n*-heptane employés à l'ébullition. Les résultats obtenus sont reportés dans le Tableau IX.

Polymérisation du propylène à température élevée. Nous avons effectué un essai de polymérisation du propylène à 80°C avec un système catalytique préparé à partir de $Al(C_2H_5)_2I$ (1 cm³), de $TiCl_3$ violet (0,8 g) et de toluène (250 cm³). Le polymère obtenu après 20 h de polymérisation à $p = 1000$ mm Hg (12 g; $[\eta] = 2{,}31$ 100 cm³/g) a été soumis à l'extraction par l'éther éthylique à l'ébullition. L'extrait (1,7% du polymère total) examiné aux rayons X, a montré une faible cristallinité due à la présence soit de produit syndiotactique que de produit isotactique.

C. Examen des Polymères

L'analyse quantitative du polypropylène, en ce qui concerne sa teneur en produit syndiotactique, n'a pas encore été mise au point.

Les polymères que nous avons préparés ont été examinés à l'infra-rouge.

L'examen infra-rouge est effectué sur des feuilles assez minces de polymère (obtenues par pressage) recuites à 100° pendant 12 h. D'après le spectre infra-rouge on détermine l'indice de syndiotacticité I_s à l'aide de la formule empirique suivante:[23]

$$I_s = \frac{11{,}53\ A}{(2{,}32\ A + 2{,}35\ A)/2}$$

A étant l'absorbance que l'on lit sur une ligne de base tracée sur deux fenêtres voisines à environ 11,4 et 11,7 μ et 2,32 A et 2,35 A étant respectivement l'adsorbance de deux bandes voisines prises comme référence, puisque leur intensité est pratiquement indépendante de la structure et de l'état physique du polypropylène. Etant donné que la bande à 11,53 μe st absente dans le polymère à l'état fondu, l'indice I_s fournit une mesure de la quantité de produit syndiotactique cristallin et non pas du simple enchaînement syndiotactique des motifs monomères.

Les spectres ont été obtenus avec un spectrographe infra-rouge Perkin-Elmer modèle 221 à optique de NaCl. La détermination de la viscosité intrinsèque des polymères a été effectuée dans la tétraline à 135°C avec un viscosimètre Desreux-Bischoff.[24]

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Résumé

Le polypropylène syndiotactique peut être obtenu par polymérisation du propylène à très basse température (par ex. $t < -70°C$) en présence de systèmes catalytiques apparemment homogènes dans les solvants hydrocarbures, préparés à partir d'un composé de vanadium (par ex. VAc_3 ou VCl_4), du AlR_2Cl et d'une base de Lewis. Les auteurs ont étudié en particulier le système VCl_4–anisole–AlR_2Cl. Les résultats les plus intéressants qui ont été obtenus peuvent être ainsi résumés: La régularité stérique du polymère que l'on obtient dépend en particulier: pour des temps égaux de polymérisation, de l'encombrement du groupe R, des rapports Al/V et V/anisole, de la température de polymérisation, et de la durée de la polymérisation. A ce sujet, les meilleurs résultats s'obtiennent en opérant à très basse température, avec de groupes R volumineux, avec des rapports Al/V $\simeq 5$ et V/anisole $\simeq 1$ et pour des temps de polymérisation assez brefs. La masse moléculaire du polymère augmente pendant la polymérisation. La vitesse de polymérisation est toujours très basse; elle diminue lorsque l'encombrement des groupes R augmente et elle dépend du rapport Al/V. Sur la base des résultats obtenus les auteurs avancent l'hypothèse que le mécanisme de la polymérisation doit être du type anionique coordiné et que les complexes catalytiques doivent contenir du VCl_2R et du $AlCl_2R$.

Synopsis

Syndiotactic polypropylene can be obtained by polymerization of propylene at very low temperature (for example at $t < -70°C$.) in the presence of apparently homogeneous catalysts in hydrocarbon mediums, prepared from a vanadium compound (as VAc_3 or VCl_4), AlR_2Cl and a Lewis base. Especially the system VCl_4-anisol-AlR_2Cl has been studied, with the following results. The stereoregularity of the polymer depends particularly from at equal duration of polymerization the steric hindrance of group R, the ratio's Al/V and V/anisol, and the duration of the polymerization. The best results are obtained by working at very low temperatures, with voluminous R-groups, with ratio's Al/V $\simeq 5$ and V/anisol $\simeq 1$, and for short times of polymerization. The molecular weight of the polymer increases during the polymerization. The rate of polymerization is always very low; it decreases when the steric hindrance of groups R increases, and it depends from the ratio Al/V. On the basis of these results it is assumed that the polymerization proceeds through a coordinated anionic mechanism, and that the catalytic complexes must contain VCl_2R and $AlCl_2R$.

Zusammenfassung

Syndiotaktisches Polypropylen kann durch Polymerisation von Propylen bei sehr tiefer Temperatur (z.B. $t < -70°$) in Gegenwart scheinbar homogener, ausgehend von einer Vanadinverbindung (z.B. VAc_3 oder VCl_4), von AlR_2Cl und einer Lewisbase dargestellter katalytischer Systeme in Kohlenwasserstoffen als Lösungsmittel dargestellt werden. Die Autoren haben besonders das System VCl_4-Anisol-AlR_2Cl untersucht. Die interessantesten der erhaltenen Ergebnisse können wie folgt zusammengefass werden: Die sterische

Regelmässigkeit des erhaltenen Polymeren hängt im speziellen für gleiche Polymerisationsdauer von der Sperrigkeit der Gruppe R; vom Verhältnis Al/V und V/Anisol; von der Polymerisationstemperatur und von der Polymerisationsdauer ab. Die besten Ergebnisse werden bei sehr tiefer Temperatur, mit grossen Gruppen R, mit einem Verhältnis Al/V $\simeq 5$ und V/Anisol $\simeq 1$ und bei genügend kurzer Polymerisationsdauer erhalten. Das Molekulargewicht des Polymeren nimmt während der Polymerisation zu. Die Polymerisationsgeschwindigkeit ist immer sehr niedrig; sie nimmt mit zunehmender Sperrigkeit der Gruppe R ab und hängt vom Verhältnis Al/V ab. Aug Grund der erhaltenen Ergebnisse sind die Autoren der Ansicht, dass der Polymerisationsmechanismus einem anionisch-koordinativen Typus entspricht und dass die katalytischen Komplexe VCl_2R und $AlCl_2R$ enthalten müssen.

Discussion

N. Plate (*Moscou, U.R.S.S.*): Avez-vous étudié les propriétés des copolymères séquencés d'éthylène et de propylène syndiotactique et est-ce que l'on peut comparer leurs propriétés avec les propriétés des polyallomères?

A. Zambelli: Notre intéret pour l'instant était seulement celui d'exclure que des complexes catalytiques différents soient responsables de la polymérisation de l'éthylène et respectivement du propylène dans le but de confirmer, en particulier, que le mécanisme n'est pas cationique. Partant, nous nous sommes limités à synthétiser un polymère contenant deux segments et nous n'avons pas étudié les propriétés de ces produits.

L. S. Rayner (*I.C.I. Ltd., Herts, Great Britain*): Have you compared the properties of your most crystalline syndiotactic polypropylene with typical isotactic polypropylenes?

A. Zambelli: La cristallinité des polypropylènes syndiotactiques que nous avons obtenus est trop inférieure à celle du polypropyléne isotactique hautement cristallin et leurs poids moléculaires sont trop bas pour qu'on puisse faire des comparaisons significatives.

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Nonbonding Interactions in the Free Propagating Methyl Methacrylate Radical

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INTRODUCTION

The study of stereospecific polymerizations has advanced to the point where, for certain systems, the various stereoregulating forces are qualitatively understood, and interest is now focussed on quantitative determinations of their magnitude. One such system is the liquid-phase, free-radical polymerization of methyl methacrylate, the stereospecificity of which appears to be insensitive to environment,[1] except perhaps in certain unusual cases.[2,3] The free radical can therefore be treated as a free propagating species,[4] and the steric interactions of the reactants, radical, and monomer, can be assessed without regard to neighboring molecules. This treatment is equivalent to the assumption that the total interaction experienced by a body in a liquid is the sum of the isolated pair interactions with each of its neighbors, each pair interaction being unaffected by the presence of the others. This pair additivity assumption is frequently used in studies of the gaseous and liquid state.

Two recent, and rather different, approaches have been made to the problem of calculating the stereoregulating forces acting on a free propagating species. Fordham[5–7] has used conformational analysis to evaluate the difference in potential energy of certain syndiotactic and isotactic vinyl polymers. The difference in the activation energies of the processes leading to these two types of polymer was then estimated using an empirical relationship between activation energy and potential energy of products derived by Evans, Gergely, and Seaman.[8]

In an attempt to obtain information more directly applicable to the transition state of the propagation reaction, Ferstandig and Goodrich[9] have examined the nonbonding forces between two propylene molecules. These authors computed the interaction energies using a modified Buckingham (exp-six) equation of the form, $E(r) = A \exp\{-br\} - C/r^6$ and found that the nonmirror superposition of the two molecules is favored. Such an approach of a monomer to a propagating chain would lead to the formation of syndiotactic polymer. The potentially useful examination of Ferstandig and Goodrich suffers from the fact that propylene does not normally polymerize by a free-radical mechanism, and they ignored the fact that sp^3

hybridization of the groups on the polymer chain alters the interaction energy.

Both these approaches suggested that the formation of syndiotactic polymer by addition of monomer to a free radical is favored over isotactic polymer by one or two kilo calories/mole, values which are in accord with those estimated from experimental measurements.[6,10,11]

Bovey[10] has used nuclear magnetic resonance to investigate a series of methyl methacrylate polymers prepared at different temperatures by a free-radical mechanism. He concludes that the activation energy for addition of a monomer unit to a free radical so as to form an isotactic placement is greater than that for a syndiotactic placement by 775 ± 75 cal./mole, and that the probability of either type of placement is governed by a single factor which is possibly the configuration of the end unit in the growing chain.

The present work represents an attempt to extend an approach similar to that of Ferstandig and Goodrich to the polymerization of methyl methacrylate, so as to determine the magnitudes of the steric effects exerted by the penultimate chain unit and the approaching monomer molecule during the propagation process. In this way it should be possible to estimate the difference in activation energy for hypothetical transition states leading to isotactic or syndiotactic placements, and to decide whether the approaching monomer or the penultimate chain unit is more important in determining stereoregularity. The uncertainty of many of the potential functions to be used, together with the complexity of the many interactions, must almost certainly cause considerably error in the absolute values obtained. However the interest in the polymerization of methyl methacrylate and the fascinating results obtained certainly seem to justify the calculation, as a semiquantitative study at least.

POTENTIAL FUNCTIONS

The modified Buckingham (exp-six) equation was first used for quantitative estimation of nonbonding interactions by Mason and Kreevoy.[12] The function has been extensively developed by Mason,[13] and a brief description together with a useful comparison with other expressions such as the Lennard-Jones (12–6) equation, has been given by Hirschfelder Curtiss and Bird.[14] Mason and Rice[15] have obtained combination rules for the interaction between unlike species, and they have also derived the interaction parameters for a number of molecules using data from second virial coefficients and transport properties. The combination rules are quite simple, essentially geometric means, and they can be expressed as follows. Consider two functions,

$$E_{11}(r) = A_{11} \exp\{-b_{11}r\} - C_{11}/r^6$$

$$E_{22}(r) = A_{22} \exp\{-b_{22}r\} - C_{22}/r^6$$

Then

$$E_{12}(r) = A_{12} \exp\{-b_{12}r\} - C_{12}/r^6$$

where $A_{12} = (A_{11}A_{22})^{1/2}$

$b_{12} = {}^1/_2(b_{11} + b_{22})$

$C_{12} = (C_{11}C_{22})^{1/2}$

These equations have considerable limitations, particularly in their range of applicability. The authors who derived them state that although they express the way in which the interaction energy varies with distance better than any previous expressions, they are best applied for $r = 2.8$ A. A comparison with the Lennard-Jones 12–6 potential for carbon monoxide interactions shows that the exp-six equation predicts larger values of the energy at separations less than 3.0 A.

In this treatment it will be assumed that interactions due to methyl groups on a molecule, bonded hydrogen atoms, and bonded carbonyl groups will be the same as those due to methane, free hydrogen atoms, and free carbon monoxide molecules, respectively, except when dipole–dipole interactions are important as with certain configurations of two carbonyl groups. There do not appear to be literature values for the interaction potential between two hypothetical ground state oxygen atoms, and it has been assumed that this potential would be similar to that between two hypothetical ground state nitrogen atoms. This latter potential has been obtained experimentally[16] in the form $E(r) = K/r^s$ which never becomes negative. It was therefore assumed that the oxygen–oxygen interaction would become zero at 3.75 A., and an exp-six expression passing through zero at this point was fitted to points on the $E(r) = K/r^s$ curve, thus allowing evaluation of the parameters A, b, C.

In only one case does an interaction involving a single carbon atom become important. This is a methyl–carbon interaction contributing about 8% of a total interaction energy. For this single case the interaction has been estimated using the methyl–oxygen interaction equation. The values of the parameters, A, b, C used for the various interactions are shown in Table I.

TABLE I
Exp-Six Parameters for Various Interactions

Interaction	A	b	C	Reference
H–H	3.72×10^3	3.07	89.5	12
Me–Me	2.74×10^5	3.33	2.94×10^3	12
(CO)–(CO)	3.47×10^6	4.15	1.93×10^3	15
O–O, (N–N)	2.17×10^3	2.21	1.53×10^3	16 (fitted)
Me–H	3.19×10^4	3.20	5.13×10^2	
Me–O	2.44×10^4	2.77	2.12×10^3	
Me–(CO)	9.75×10^5	3.74	2.38×10^3	
H–O	2.84×10^3	2.64	3.70×10^2	
H–(CO)	3.59×10^5	3.62	4.16×10^2	
O–(CO)	8.69×10^4	3.18	1.76×10^3	

Electrostatic interactions were calculated using the equation

$$U(r) = (-\mu_a\mu_b/r^3)(2\cos\theta_a\cos\theta_b - \sin\theta_a\sin\theta_b\cos\phi)$$

where $\theta_a\theta_b$ are the angles between the dipoles and the line joining their centers, ϕ is the angle between two planes, one through each dipole, intersecting along the line of center. Dipole–dipole interactions were calculated for carbonyl–carbonyl interactions only, using a value[17] of 2.7 D for the dipole moment of the carbonyl group. Dipole effects due to polarization of the electron pairs on the C—O—C oxygen atom were ignored.

At the intermolecular configurations of minimum potential energy the position of the minimum is rather insensitive to the form of the interaction potentials used, and qualitatively meaningful results can be obtained from any values of A, b, C correct to an order of magnitude. In this region of minimum interaction, too, the individual potentials change only slowly with separation so that errors in the estimation of internuclear separations are minimized, and errors in the computed energy are similar in magnitude to errors in A, b, C.

MOLECULAR GEOMETRY

The detailed molecular structure of methyl methacrylate monomer has been determined by Ukaji[18] from electron diffraction measurements. Most of the molecular parameters can be described by standard bond lengths and angles. The main feature of the work is that the molecule is planar, except for the methoxy group which lies at an angle of 25° out of the plane containing the C=C and C=O, bonds.

In the present work models of the polymethyl methacrylate radical and the monomer unit were constructed using Dreiding stereomodels (scale 0.4 A./cm.) which had standard bond lengths and angles.—The models were mounted on a rigid framework so that measurements of the internuclear distances could be made with either internal or external callipers. The measurements were reproducible to ±0.1 A. In one of the simpler arrangements of monomer unit and free radical the internuclear distances were calculated trigonometrically and agreed with those measured to within ±0.1 A.

The intermolecular arrangements examined are those which might exist immediately prior to, and immediately after, addition of a monomer unit to a free radical. All the arrangements are based upon a picture of the addition process whereby the unpaired electron in a p-orbital of the polymeric free radical is able to overlap with either the π-orbital of the monomer, or a p-orbital of the monomer methylene group.

a. Terminal Unit–Penultimate Unit Geometry

Two possible arrangements were examined, one in which the methyl groups lie on the same side of the carbon backbone chain, called case I, and one in which they lie on opposite sides, called case II. These two ar-

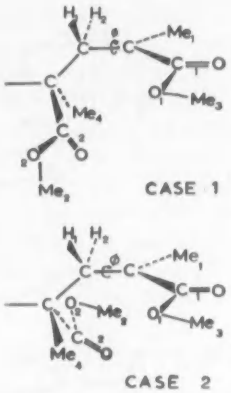

Fig. 1. Terminal unit–penultimate unit geometry.

rangements are illustrated in Figure 1. The arrangement of the penultimate ester unit is hard to determine, and several possibilities taking the anti-penultimate unit into account were studied. Changes in hybridization of the terminal carbon atom from sp^2 to sp^3 force the substituents on this atom into closer proximity with those on the penultimate unit.

b. Monomer–Terminal Unit Geometry

A series of arrangements of the monomer unit and the radical end were examined. In all cases the monomer unit was first set in a plane parallel with that containing the terminal carbon atom and its substituents. The ester group attached to the free radical carbon atom was assumed to have the same conformation as in the monomer,[18] and the CH_2—$\dot{C}$ bond length was taken as 1.54 A.

The first arrangement considered, case III, was formed with the methyl groups of the terminal unit and of the monomer on the same side of the incipient carbon backbone, Figure 2. This situation is equivalent to the "mirror" case of Ferstandig and Goodrich. Two subcases were examined to obtain a comparison between the two possible forms of electronic orbital overlap which could lead to bond formation. The first subcase was taken with the CH_2 group of the monomer unit directly over the radical end (i.e., the value of x in Figure 2 is zero). This situation, corresponding to a transition state involving overlap of the radical p-orbital with a localized p-orbital of the monomer will be termed the p-σ subcase. In the second subcase the midpoint of the monomer double bond is situated above the radical end carbon atom (x = 0.66 A. in Figure 2). In this system the possible overlap is between the p-orbital of the radical and the π-bond of the monomer, and the system is termed the p-π subcase. Values of x intermediate between the two subcases have also been considered, and the change in total interaction energy between the two subcases is always regular. In

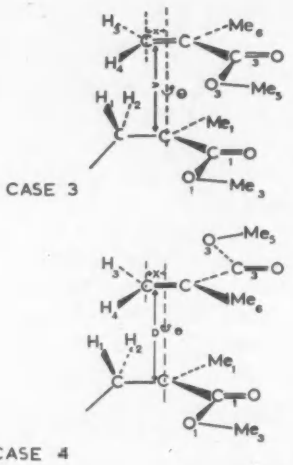

Fig. 2. Terminal unit–monomer geometry.

the p-π subcase maximum overlap is possible with the monomer plane not parallel to the plane of the terminal unit, so long as the intersection of the two planes is perpendicular to the direction of the CH_2—$\dot{C}$ bond. This subcase is first examined in detail with the planes parallel, and then some consequences of the tilting are discussed.

The second arrangement, case IV, contained the methyl groups of the radical and monomer on opposite sides of the incipient carbon chain, and is equivalent to the "nonmirror" case of Ferstandig and Goodrich.

For each subcase, p-σ and p-π of orientations III and IV, measurements of internuclear distances were made at a series of angular displacements, θ, of the monomer unit about an axis perpendicular to each of the parallel planes and passing through the radical carbon atom. The main values of θ at which measurements were made were 0°, 30°, 60°, 90°, 270°, 300°, 330°, where 0° is the case when the CH_2—$C(CH_3)(COOCH_3)$ carbon-carbon bonds are parallel. Further internuclear separations were measured at values of θ near important minima in the total value of the interaction energies. Monomer approaches characterized by values of θ between 90° and 270° lead either to head-to-head addition or to improbably high interaction energies.

Four separations, d, of the monomer unit and the radical end were examined: 2.0, 2.4, 3.0, and 3.4 A. It was soon evident that the 2.0′ and 2.4 A. separations of the two planes were unrealistic, as the values of $E(r)$ were greater than the bond dissociation energies for some single interactions. The 3.0 A. separation was considered sufficiently large to represent the conditions between the monomer unit and the radical end before the transition state had been reached. The 3.0 A. separation, unlike the 3.4 A. separation is still small enough to show the pertinent repulsive interactions

between the various groups, and the internuclear distances have values for which the energy equations are most reliable.

Systems in which the monomer unit approaches the terminal unit from the same side as the penultimate groups ("underneath" in Figure 2) were found to involve improbably large steric repulsions, despite the fact that such an "above-beneath-above" chain formation would lead most easily to the 5_2 or 10_4 chain helix described by Stroupe and Hughes[19] for crystalline polymethyl methyacrylate. In the "above-above" addition implied in cases III and IV, interactions between the penultimate group and the monomer are negligible, so that it is possible to consider cases III and IV separate from cases I and II, and then to obtain the interaction energies for the four possible combinations by the relevant additions.

INTERACTION ENERGIES

a. Terminal Unit–Penultimate Unit Interactions

In general the penultimate ester group experiences minimum interactions when the carbonyl C=O bond lies at an angle of 80° with the plane of the terminal unit, and the O—Me bond is perpendicular to this plane.

In case II it was found that the minimum total energy occurred with the two CH_2—C(Me)(COOMe) bonds parallel, but in case I the energy minimum involved a rotation of 30° about the bond joining the penultimate monomer unit to the methylene of the terminal monomer unit. At the position of minimum energy the interactions on each side of the backbone chain are equal.

The relevant interactions for various angles of rotation, ϕ, of the terminal C(Me)(COOMe) sp^2 hybridized group, are listed in Table II.

Complete rotation of the terminal unit is hindered by energy barriers greater than 20 kcal./mole, and two stable rotational isomers occur at 0° (case II) and 206° (case I) rotation. The interaction energies for the two

TABLE II
Penultimate Unit–Terminal Unit Interaction Energies for an sp^2-Hybridized Terminal Carbon Atom

Interacting groups	Interaction energy, kcal.				
	Case I				Case II,
	195°	200°	210°	220°	0°
Me_1–Me_4	3.0	3.9	6.3	13.1	0.0
Me_1–O_2	0.0	0.0	0.0	0.0	2.4
Me_1–$(CO)_2$	0.0	0.0	0.0	0.0	0.1
Me_4–$(CO)_1$	0.0	0.0	0.0	0.0	0.1
Me_4–O_1	0.0	0.0	0.0	0.0	2.4
O_1–$(CO)_2$	4.0	3.2	0.5	0.0	0.0
O_1–O_2	0.8	0.4	0.2	−0.1	0.0
Total	7.8	7.5	7.0	13.0	5.0

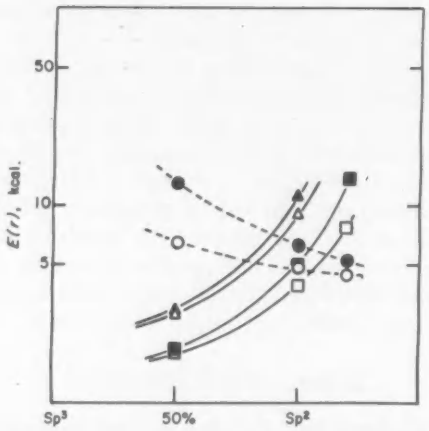

Fig. 3. Minimum interaction energies for (- -) terminal unit–penultimate unit interactions: (●) case I, (○) case II; (——) terminal unit–monomer interactions: (■) case III with p-π orbital overlap, (□) case IV with p-π orbital overlap, (▲) case III with p-σ orbital overlap, (△) case IV with p-σ orbital overlap.

stable states are plotted against a percentage change in sp^2-sp^3 character of the terminal carbon atom in Figure 3. The change is defined as varying linearly with the angular displacement of the substituent groups as the bond angle changes from 120° to 109°. The curves of Figure 3 are continued past the point of 100% sp^2 character in order to illustrate the situation when the substituents on the terminal carbon atom are displaced away from the substituents on the penultimate unit, but into the path of an approaching monomer unit. The low energy difference between cases I and II at these displacements is relevant for the existence of a free-radical in the absence of monomer as might be obtained by irradiation of polymer, but not to the propagating radical during monomer addition.

b. Terminal Unit–Monomer Interactions

The number of measurements is considerable, so that only a selection of the individual energies for values of θ near important minima have been recorded in Tables III and IV, the complete results being shown graphically in Figures 4 and 5.

In the p-σ subcases the optimum approach of a monomer unit to the free radical occurs with $\theta = 32°$ for case III and $\theta = 40°$ for case IV, the latter case being favored by 800 cal./mole when the intermolecular separation is 3.0 A. If the addition reaction proceeds by way of p-π overlap, the energy minima occur at $\theta = 87°$ for case III and $\theta = 54°$ for case IV, the latter again being of lower energy by 1.2 kcal./mole. In view of the limitations of the calculation it is difficult to make a precise comparison of the energies involved in the p-σ and p-π subcases. The values are close enough to sug-

TABLE III
Terminal Unit–Monomer Interaction Energies for Case III at an Intermolecular Separation of 3.0 A.

Interacting groups	Interaction energy, kcal. $\theta = 20°$, $x = 0.0$	$\theta = 30°$, $x = 0.0$	$\theta = 40°$, $x = 0.0$	$\theta = 90°$, $x = 0.66$
Me_1–Me_6	3.9	1.4	1.4	0.0
Me_3–Me_5	−0.3	0.0	0.0	0.0
O_3–Me_3	0.6	0.1	0.0	0.0
O_1–O_3	0.0	0.0	0.0	0.0
$(CO)_1$–O_3	1.0	1.6	1.0	0.0
$(CO)_3$–Me_1	−0.3	−0.2	0.3	4.0
$(CO)_1$–H_4	0.2	0.7	2.1	4.7
$(CO)_2$–$(CO)_1$	1.1	0.3	0.0	0.0
H_1–H_4	0.5	0.4	0.1	0.0
H_1–H_3	0.3	0.4	1.0	0.4
H_2–H_4	0.0	0.0	0.0	0.0
H_2–H_3	0.5	0.3	0.3	0.0
H_3–Me_1	0.0	0.0	0.0	0.0
H_4–O_1	0.0	0.1	0.1	0.2
H_2–Me_6	0.0	0.0	0.0	0.4
O_3–Me_1	0.0	0.0	0.0	0.4
Total	7.4	5.1	6.3	10.2

TABLE IV
Terminal Unit–Monomer Interaction Energies for Case IV at an Intermolecular Separation of 3.0 A.

Interacting groups	Interaction energy, kcal. $\theta = 30°$, $x = 0.0$	$\theta = 40°$, $x = 0.0$	$\theta = 50°$, $x = 0.0$	$\theta = 45°$, $x = 0.66$	$\theta = 60°$, $x = 0.66$
Me_1–Me_6	0.0	0.1	1.5	0.5	2.4
Me_6–$(CO)_1$	0.7	0.0	0.0	0.7	0.0
Me_1–$(CO)_3$	1.3	0.7	1.3	4.0	1.3
Me_1–O_3	0.6	0.0	0.0	0.0	0.0
Me_1–H_3	0.0	0.1	0.1	0.0	0.0
H_1–H_3	1.0	0.7	1.0	1.0	2.0
H_1–H_4	0.1	0.0	0.0	0.3	0.0
H_2–H_3	0.5	0.1	0.3	0.1	0.0
H_2–H_4	0.1	0.0	0.0	0.0	0.0
H_4–$(CO)_1$	1.4	2.1	3.1	1.4	2.1
H_4–O_1	0.1	0.1	0.1	0.3	0.1
H_2–O_3	0.0	0.1	0.4	1.0	1.8
Total	5.8	4.0	7.8	9.7	9.8

gest that the energy difference between the two monomer configurations is of the order of 1 kcal./mole irrespective of subcase. The dependence of the minimum interaction energy on the hybridization of the terminal carbon atom is illustrated in Figure 3, and the dependence of the energy difference between case III and case IV for the *p-n* subcase is given in Table V.

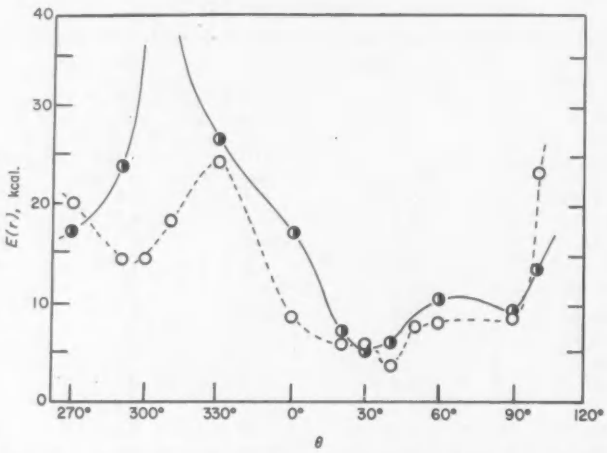

Fig. 4. Terminal unit–monomer interaction energies, p-π orbital overlap, d = 3.0 A.: (◑) case III; (○) case IV.

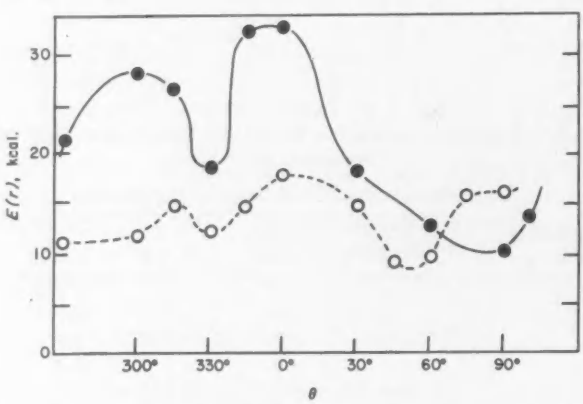

Fig. 5. Terminal unit–monomer interaction energies, p-σ orbital overlap, d = 3.0 A.: (●) case III, (○) case IV.

TABLE V

Variation of the Energy Difference between Case III and Case IV with Intermolecular Separation

Intermolecular separation d, A.	$E(r)_{III} - E(r)_{IV}$, Kcal./mole
2.6	11.1
2.8	4.0
3.0	0.8
3.2	0.3
3.4	0.1

DISCUSSION

Evaluation of the difference in activation energy between the possible stereo types of propagation reaction (the ultimate aim of a calculation such as this) cannot be obtained uniquely because the intermolecular separation of the monomer and radical in the transition state remains an unspecified variable. This separation, representing a position of maximum total energy, can only be obtained by consideration of both the bonding electronic interactions and the nonbonding or steric interactions considered above. While all the results presented in this paper cannot, therefore, be directly checked experimentally, they may be used in conjunction with certain experimental observations to predict some properties of the transition state.

Perhaps the most significant result of the calculation is the magnitude of the energy barrier preventing rotation of the terminal —$\dot{C}(CH_3)(COOCH_3)$ group. As a result of this barrier, propagation is much more rapid than rotation, and the configuration of the penultimate unit–terminal unit in the transition state as the next monomer approaches is a direct consequence of the mode of addition of the last monomer unit. Thus the stereochemistry of the growing polymer chain can be discussed in terms of the approach of a monomer molecule.

If the transition state of the propagation step does not involve any alteration in the hybridization of the terminal carbon atom, the activation energies and the relative probabilities of the two stereoadditions will depend only on the monomer–terminal unit interactions, and the two probabilities can be described by a single parameter. However, if the transition state is formed with some increase in the sp^3 character of the terminal carbon atom, the energy increments due to terminal unit–penultimate unit interactions will depend on the conformation of the penultimate unit. It will then be necessary to distinguish four stereo types of propagation reaction, formation of isotactic, heterotactic (terminal carbon and monomer with the same potential asymmetry), heterotactic (polymer chain carbon atoms with the same potential asymmetry but monomer with opposite potential asymmetry) or syndiotactic triads; the nomenclature for triads was first suggested by Bovey.[10] Under these circumstances two parameters are necessary to describe the probability of any sequence occurring in the growing polymer chain. Experimental observations of the stereoregularity of polymethyl methacrylate prepared by free-radical methods[10,11] have suggested that the probability of any stereoaddition is governed by a single parameter, symbolized as α by Coleman[24] and σ by Bovey.[10] From this it must be inferred that changes in the hybridization of the free-radical carbon atom as it enters the transition state are slight.

In a different approach to the problem of carbon atom hybridization in such a transition state, Szwarc[20] has studied the kinetic isotope effect in the polymerization of β-deutero-styrene, and has concluded that the methylene carbon atom of the monomer gains approximately 20% sp^3 character

in the change monomer to transition state. A similar slight change in the hybridization of the terminal carbon atom during the propagation of methyl methacrylate would imply that the penultimate unit does exert some influence, but that the energy differences involved would only be 20–30% of those caused by the monomer configuration. Under these conditions a probability treatment based on a single parameter will not be exactly correct.

The large energy barriers to rotation of the terminal group suggest that in the absence of propagation two rotational isomers (0° and 206°) should coexist. Electron spin resonance studies of polymethyl methacrylate radicals[21] indicate the presence of two types of radical, one interpretation of which could be the existence of rotational isomers. On this interpretation the spectra can be analyzed to suggest that the isomers correspond to 0° and 195° rotation in reasonable agreement with the results derived above. The relative populations of the two isomeric states can be estimated from the energy difference of 1.5 kcal./mole for conditions when the two forms are in equilibrium.

The difference in activation energy for the two types of stereoaddition has been estimated as 0.775 kcal./mole[10] and 1.07 kcal./mole.[11] Comparison of these values with the interaction energies computed here suggests an intermolecular separation, d, in the transition state of approximately 3.0 A., a separation significantly larger than the 2.6 A. chosen for the propylene cases by Ferstandig and Goodrich.[9]

Determination of the activation energy difference from an exact kinetic measurement of temperature dependence of the total propagation rate is likely to prove extremely difficult. Semenov[22] has reported a decrease in the measured activation energy for propagation as the temperature is lowered. The decrease calculable from the curvature of the ln k_p versus $1/T$ plot reproduced by Semenov is much greater than is compatible with that inferred by the nuclear magnetic resonance measurements.[10,11] Semenov rejects the explanation that the effect is due to an alteration in the relative importance of two concurrent propagation reactions, and suggests instead that it is due to an energy chain reaction in pseudo-crystalline regions of the monomer. This hypothesis has been tested at 60°C.,[11] and at the more relevant temperatures below 0°C. by kinetic measurements[23] and by examination of the stereoregularity of polymer formed in a variety of solvents,[1] and it does appear that Semenov's explanation is not applicable to this case.

Preliminary measurements in this laboratory using a rotating sector technique have yielded surprisingly high radical lifetimes, and it is obvious that a detailed kinetic study of the termination reaction must also be made before it is possible to even attempt kinetic evaluation of the activation energy for propagation at low temperatures.

In conclusion, then, it can be stated that the calculation presented above is useful in predicting semiquantitatively that syndiotactic addition takes place with a lower energy of activation than does isotactic addition. For a

transition state in which the monomer and radical planes are separated by 3.0 A. and in which the free radical does not become appreciably sp^3 hybridized, the probability of either addition can be discussed in terms of a single parameter, α, and $RT[d \ln(\alpha/1 - \alpha)/d \ln T]$ is approximately 1 kcal./mole.

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Synopsis

A study has been made of the interactions between the nonbonding groups of a free-propagating polymethyl methacrylate radical in an attempt to predict the relative rates of syndiotactic and isotactic monomer placement. A modified Buckingham (exp-six) equation, $E(r) = A \exp\{-br\} - C/r^6$ has been used to evaluate (*a*) interactions between the penultimate monomer unit and the substituents on the free-radical carbon atom as a function of the rotation of the terminal —$\dot{C}(CH_3)(COOH)$ group and (*b*) interactions between an approaching monomer molecule and the terminal —CH_2—$C(CH_3)(COOH)$ unit as a function of the molecular separation, the angle between the two CH_2—C carbon–carbon bonds, the relative configurations of the substituted carbon atoms, and the type of orbital overlap in an incipient transition state. Calculations of this type can, at present, be considered only as semiquantitative, but they do predict that, rotation of the terminal —$\dot{C}(CH_3)(COOH)$ group is hindered by energy barriers greater than 20 kcal./mole. Two stable states exist when the terminal methyl group neighbors the penultimate ester group, 0° rotation, and when the terminal methyl group is rotated slightly away from the penultimate methyl, 206° rotation. The former state, leading to a syndiotactic diad, is preferred by about 1.5 kcal./mole, which value increases with increasing sp^3 hydridization of the terminal carbon atom. Also, both for p-σ and p-π overlap in an incipient transition state the monomer approach leading to a syndiotactic

diad is favored. The energy difference between the two possible approaches ranges from 1 kcal./mole for 3.0 A. separation to 20 kcal./mole for 2.4 A. separation. The results imply that at sensible monomer concentrations propagation is more rapid than terminal unit rotation, leading to retention of configuration, and that the probability of either stereoisomeric monomer placement can therefore be described by a single parameter if the transition state involves no appreciable increase in sp^3 hybridization of the free radical. Experimental observations of polymer tacticity and propagation rate are discussed in the light of these findings.

Résumé

On étudié les interactions entre les groupes non-liés d'un radical de polyméthacrylate de méthyle se propageant librement en vue de prédire les vitesses relatives du placement isotactique et syndiotactique du monomère. On a employé une équation modifiée de Buckingham (exp-six): $E(r) = A \exp\{-br\} - C/r^6$, pour évaluer (*a*) les interactions entre la pénultième unité de monomère et les substituants sur l'atome de carbone du radical libre en fonction de la rotation du groupe —C(CH_3)(COOH) terminal; (*b*) les interactions entre une molécule de monomère et l'unité terminale —CH_2—C(CH_3)(COOH) en fonction de la séparation moléculaire, de l'angle entre les deux liens carbone-carbone CH_2—C des configurations relatives des atomes de carbone substitués, et du type de recouvrement des orbitales au début de l'état de transition. A présent les calculs de ce type doivent être considérés comme semi-quantitatifs, mais ils permettent de prédire que: (*a*) la rotation du groupe terminal —C(CH_3)(COOH) est empêchée par une barrière d'énergie supérieure à 20 kcal/mole. Il existe deux états stables: quand le groupe méthy le est au voisinage du pénultième groupe ester, 0° de rotation, et quand le groupe méthyle terminal est détourné légèrement du groupe méthyle pénultième, 206° de rotation. Le premier état, qui mène à une structure syndiotactique, est avantagé de 1.5 kcal/mole. Cette valeur augmente quand l'hybridation sp_2 de l'atome de carbone terminal augmente. (*b*) aussi bien pour le recouvrement p-σ que pour le recouvrement p-π au début de l'état de transition, le rapprochement du monomère menant à une structure syndiotactique est favorisé. La différence d'énergie entre les deux rapprochements possibles est comprise entre 1 kcal/mole pour une séparation de 3 A et 20 kcal/mole pour une séparation de 2.4 A. Ces résultats impliquent que, à des concentrations sensibles de monomère, la propagation est plus rapide que la rotation de l'unité terminale, menant ainsi à une rétention de configuration. La probabilité des placements stéréoisomères du monomère peut donc être décrite par un seul paramètre à condition que l'état de transition n'augmente pas sensiblement l'hybridation sp_2 du radical libre. Tenant compte de ces résultats, on discute les observations expérimentales de la tacticité des polymères de la vitesse de polymérisation.

Zusammenfassung

Eine Untersuchung der Wechselwirkung zwischen den nicht-bindenden Gruppen eines frei-wachsenden Polymethylmethacrylatradikals wurde durchgeführt, um Aussagen über die relative Geschwindigkeit der syndiotaktischen und isotaktischen Monomer-Plazierung zu ermöglichen. Eine modifizierte Buckingham-(exp-sechs)-Gleichung, $E(r) = A \exp\{-br\} - C/r^6$ wurde zur Ermittlung folgender Grössen verwendet: (*a*) die Wechselwirkung zwischen der vorletzten Monomereinheit und den Substituenten am radikalischen Kohlenstoffatom als Funktion der Rotation der endständigen —Ċ(CH_3)(COOH)-Gruppe; (*b*) die Wechselwirkung zwischen einem herantretenden Monomermolekül und der endständigen —CH_2—C(CH_3)(COOH)-Einheit als Funktion des Molekülabstands, des Winkels zwishcen den beiden CH_2—C-Kohlenstoff-Kohlenstoffbindungen, der relativen Konfiguration der substituierten Kohlenstoffatome und des Orbital-Überlappungstyps bei Erreichung des Übergangszustandes. Derartige Berechnungen können gegenwärtig zwar nur als halb-quantitativ betrachtet werden,

sie gestatten aber immerhin die Aussage, (*a*) dass die Rotation der endständigen —Ċ(CH$_3$)(COOH)-Gruppe durch eine Energieschranke von mehr als 20 kcal/Mol gehindert wird und daher zwei stabile Zustände bestehen, einer bei Nachbarschaft der endständigen Methylgruppe zur vorletzten Estergruppe, 0° Rotation, und einer bei schwacher Rotation der endständigen Methylgruppe in Richtung von vorletzten Methyl, 206° Rotation; ersterer Zustand, der zu einer syndiotaktischen Diade führt, ist um 1,5 kcal/Mol günstiger, welcher Wert mit steigender sp^2-Hybridisierung des endständigen Kohlenstoffatoms zunimmt; (*b*) dass sowohl bei p-σ-als auch p-π-Überlappung im beginnenden Übergangszustand die zur syndiotaktischen Diade führende Monomerannäherung begünstigt ist. Der Energieunterschied zwischen den beiden möglichen Annäherungsweisen liegt zwischen 1 kcal/Mol für einen Abstabd von 3,0 A und 20 kcal/Mol für einen solchen von 2,4 A. Die Ergebnisse bedeuten, dass bei merkbarer Monomerkonzentration das Wachstum schneller verläuft als die Rotation der Endgruppe, was zu einer Konfigurationsretention führt, und dass die Wahrscheinlichkeit jeder stereoisomeren Monomerplazierung daher durch einen einzigen Parameter beschrieben werden kann, vorausgesetzt, dass im Übergangszustand keine merkliche Zunahme der sp^2-Hybridisierung des freien Radikals auftritt. Die Versuchsergebnisse bezüglich der Polymertaktizität und Wachstumsgeschwindigkeit werden im Lichte dieser Befunde diskutiert.

PROPERTIES OF BLOCK AND GRAFT COPOLYMERS IN SOLUTION

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Theory of the Thermodynamic Properties of Solutions of Graft and Block Copolymers

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Introduction

The theory of the thermodynamic properties of dilute polymer solutions which was first independently developed by Flory and the writer and extended by many others has proven useful (*1*) in interpreting, qualitatively and semiquantitatively, the behavior of both dilute and nondilute solutions. (*2*) in the determination of average molecular weights from experimental data, (*3*) in leading to the obtaining of so-called "interaction constants" characteristic of the polymer–solvent systems, and in other ways.[1]

This theory, developed for dilute solutions, has not been quantitatively satisfactory at higher concentrations. Moreover, it has not enabled a very close correlation between the interaction constants and other experimental functions, on the one hand, and molecular properties (sizes, shapes, flexibilities, interaction energies, etc.), on the other. For a number of years the writer has been trying to remedy these deficiencies. Some of the results of his efforts in this direction have been published.[2] The present paper constitutes a further progress report.

Previously, the thermodynamic properties have been expressed, at least in part, as a power series in the concentration, usually expressed as the volume fraction of polymer in the solution. Now, with the aid of certain assumptions and approximations which appear reasonable, it has proven possible to replace the power series with equations in closed form. If the new equations prove to be sufficiently accurate, it will be possible to deduce the thermodynamic properties at intermediate and high concentrations with the aid of a few constants determined at relatively low concentrations.

In the new equations the experimental variables are related directly to molecular and intermolecular properties. If they prove satisfactory, it should be possible to determine experimentally the molecular quantities for systems of interest and, eventually, to deduce the thermodynamic data for unknown systems for which the pertinent molecular properties are known.

The new equations are of such form that they can readily be applied to systems containing two or more types of solvent, and/or two or more types

of polymer, either present as homopolymer molecules, or as copolymer molecules (block, graft, random, etc.). In dealing with such cases, the molecular functions entering into the equations must, of course, be appropriately averaged.

Outline of the Theory for Solutions of Homopolymers

We are concerned primarily with the partial molal free energies of mixing and the related partial molal heats and partial molal entropies for the solvent (component 1):

$$\Delta\bar{F}_1 = \Delta\bar{H}_1 - T\Delta\bar{S}_1 \tag{1}$$

As normally used, these changes are for constant pressure. The corresponding relation for constant volume is

$$\Delta\bar{A}_1 = \Delta\bar{E}_1 - T(\Delta\bar{S}_1)_V \tag{2}$$

Theoretically, it is simpler to deal with the constant volume case, i.e., to assume no volume change on mixing the components, and this will be done in this paper. The approximation that $\Delta\bar{A}_1$ and $\Delta\bar{F}_1$ are equal is sufficiently accurate for most purposes.

The energy of a two-component solution can be related to hypothetical "molecular surface areas" of the component molecules, to the concentration dependence of the fractions of these areas which are in contact with surfaces of molecules of the other kind, in contact with surfaces of other molecules of the same kind, in contact with other portions of the surface of the same molecule, and in contact with no other molecular surface. The energies of interaction per unit contact area, of three types (polymer–polymer, polymer–solvent, and solvent–solvent) are, of course, important. Allowance must obviously be made for the dependence of the relative probabilities of contacts of the various kinds of the relative magnitudes of the three types of attraction energies per unit contact area.

It is necessary to introduce a shielding function, to allow for the fact that the interior segments of a convoluted molecule are partially shielded from contact with interior segments of other polymer molecules. Moreover, allowance must be made for the increased probability of a second (or third, etc.) contact between two polymer molecules, as a result of there being one contact between them.

Putting these ideas on a mathematical basis, the writer has deduced[3] the relation

$$\frac{\Delta E_1}{RT} = \mu_e V_2^2 = \mu_e^\circ \left\{ \frac{f_{sh}\left[1 + m\left(\frac{1 - f_{sh}}{f_{sh}}\right)V_2\right]}{k_{sh}[1 - (1 - k_{ext}k_{mic}f_{sh}W)V_2]^2} \right\} V_2^2 \tag{3}$$

with

$$\mu_e^\circ = (\bar{V}_1/\bar{V}_2)\,KWL \tag{4}$$

$$K = k_{ext}k_{mc}k_{sh} \tag{5}$$

$$W = \exp\{k_\sigma \Delta\epsilon/k_B T\} \tag{6}$$

$$L = \sigma_2' \Delta\epsilon/k_B T \tag{7}$$

$$\Delta\epsilon = 2\epsilon_{21} - \epsilon_{11} - \epsilon_{22} \tag{8}$$

$$f_{sh} = 1 - (1 - k_{sh})V_1^m \tag{9}$$

Here, V_1 and V_2 are the volume fractions of solvent and solute, respectively, in the solution.

μ_e is the energy part of the interaction function, which has been designated as μ by the writer and χ by Flory; μ_e° is the limiting value of μ_e at infinite dilution.

f_{sh} is the shielding function, of such a form that it has the value k_{sh} at infinite dilution and approaches unit as V_1 approaches zero. The rate at which the shielding changes with concentration is governed by m. Although constant for a given system of solvent and polymer (with given molecular weight and molecular weight distribution) at a given temperature, k_{sh} would be expected to depend markedly on the molecular weight of the polymer and on the interaction energies, ϵ, and the temperature, T. The value of m presumably also depends on these variables.

k_{ext} is the average fraction of contacted polymer molecule surface which is in contact with surfaces of other molecules.

k_{mc} is a multiple contact factor, measuring the increased probability of two or more contacts, mentioned above.

σ'_2 is the effective surface area per polymer molecule, not counting the area in contact with other portions of the same molecule or with no other surface.

ϵ_{21}, ϵ_{11}, and ϵ_{22} designate interaction energies, per unit area of contact, for the three types of intermolecular contacts.

k_σ is a proportionality constant in the exponential factor relating the relative probabilities of contacts of the three types to their different contact energies.

k_B and R are the Boltzmann constant and the molal gas constant, respectively.

The entropy of a high polymer solution can be computed by considering first the entropy of placing the solvent molecules and the first segments of the solute molecules in the total volume, making due allowance for departures from perfect randomness resulting from differences in the contact energies for contacts of the three different types, and then considering the entropy associated with the randomness of orientation of each rigid segment relative to the preceding segment, in the solute molecules. Obviously, the molecular and segment volumes and the numbers of rigid segments are involved. With regard to the orientations of successive segments, the important function is that relating the degree of orientation randomness and the concentration.

The quantitative treatment leads to the following equation for the partial molal entropy of mixing, $\Delta\bar{S}_1$:

$$\frac{(\Delta\bar{S}_1)_V}{R} = \frac{\bar{V}_1}{\bar{V}_2} V_2 + n_r \frac{\bar{V}_1}{\bar{V}_2}\frac{V_2}{V_1}\left[1 + m\left(\frac{1 - f_{sh}}{f_{sh}}\right) V_2\right] \left\{\frac{\ln\left[1 + (1 - k_s)k_{ext}k_{mc}f_{sh}W\frac{V_2}{V_1}\right] - (1 - k_s)\ln\left[1 + k_{ext}k_{mc}f_{sh}W\frac{V_2}{V_1}\right]}{(1 - k_s)k_{ext}k_{mc}f_{sh}W\frac{V_2}{V_1}}\right\} \tag{10}$$

Here, $\bar{V}_1$ and $\bar{V}_2$ are the partial molal volumes of solvent and solute, n_r is the average number of rigid segments per molecule, and k_s is a proportionality constant relating the average decrease in the randomness of orientation of a polymer segment (relative to the preceding segment) to the probability of contact between the segment surface and the surface of another polymer molecule.

The partial molal entropy of mixing is related to the entropy part of the interaction function μ by the equation:

$$\mu_s = \frac{1}{V_2^2}\left[\ln V_1 + \left(1 - \frac{\bar{V}_1}{\bar{V}_2}\right) V_2 - \frac{(\Delta\bar{S}_1)_V}{R}\right] \tag{11}$$

The interaction function, $\mu = \mu_e + \mu_s$, is in turn related to the partial molal free energy of mixing (assuming no volume change on mixing) by the equation:

$$\frac{\Delta\bar{F}_1}{RT} = \ln V_1 + \left(1 - \frac{\bar{V}_1}{\bar{V}_2}\right) V_2 + \mu V_2^2 \tag{12}$$

Since the experimental (thermodynamic) properties of interest can be directly and quantitatively related to ΔF_1, we thus have a theoretical connection between these properties and the molecular properties. It is planned to deal with experimental tests of these theoretical relationships and with applications to different types of polymers in a later paper or papers.

Theoretical Extension to Copolymers

Let us now consider solutions of copolymers, the molecules of which are composed of mers of two types, which we shall distinguish by the subscripts a and b. Let there be n_a mers of type a and n_b mers of type b, per molecule, on the average. These two types of mers will contribute different amounts to the molecular volume, the molecular surface, the interaction energies, the restriction of orientation at the flexible joints of the molecules, and other quantities entering into the theory and the equations described above. We must consider, quantitatively if possible, how these quantities depend on their magnitudes for the two types of homopolymer (all a-mers and all b-mers), on the relative number of the

two types and on their distribution within the molecules. We shall deal primarily with an assumed random distribution, discussing only briefly and qualitatively the effect of such nonrandomness of mer distribution as is found in graft and block copolymers.

The molecular volume of the polymer [see eq. (4)] is given by the equation

$$V_2/N_A = n_a v_a + n_b v_b \tag{13}$$

where N_A is Avogadro's number and v_a and v_b are the average contributions of the two types of mer. Similarly, the molecular surface is composed additively of contributions of the two types of mer. The ratio between the mer surface and the mer volume is of the order of $2/r_a$ or $2/r_b$ (the values for hypothetical cylindrical mers of radius r_a and r_b, neglecting the unoccupied volume between molecules). This ratio, which we shall designate as $k_{a,\sigma/v}$ and $k_{b,\sigma/v}$ for the homopolymers a and b, can reasonably be expected to be practically constant, for each type of mer, in copolymers. Therefore,

$$\sigma_2 = \sigma_{2,a} + \sigma_{2,b} \tag{14}$$

with

$$\sigma_{2,a} = k_{a,\sigma/v}\, n_a v_a \tag{15}$$

$$\sigma_{2,b} = k_{b,\sigma/v}\, n_b v_b \tag{16}$$

If we assume that the fraction of the molecular surface of type a which is in contact with other portions of the same molecule and the fraction which is not in contact with any molecular surface are both independent of the relative numbers of a- and b-mers and of their distribution within the molecules, and likewise for the molecular surface of type b, the average surface area per molecule which is in contact with the surfaces of other (solvent or solute) molecules is

$$\sigma'_2 = \sigma'_{2,a} + \sigma'_{2,b} \tag{17}$$

with

$$\sigma'_{2,a} = k_{a,\sigma/v}\, k_{a,\sigma'/\sigma}\, n_a v_a \tag{18}$$

$$\sigma'_{2,b} = k_{b,\sigma/v}\, k_{b,\sigma'/\sigma}\, n_b v_b \tag{19}$$

Here, $k_{a,\sigma'/\sigma}$ and $k_{b,\sigma'/\sigma}$ are the ratios σ'_2/σ_2 for the two types of homopolar polymers.

With the same assumptions the constant k_{ext} for the copolymer can be related to the corresponding constants for the homopolymers and to the σ'_2 values for the homopolymers by the equation

$$k_{ext} = \frac{\sigma'_{2,a} + \sigma'_{2,b}}{\alpha_\sigma(\sigma_{2,a} + \sigma_{2,b})} \tag{20}$$

where α_σ is the fraction of the surface of a polymer molecule which is in contact with other molecular surfaces, of any kind.

In previous treatments the writer has suggested that the multiple contact factor, here called k_{mc}, can be approximately represented by the relationship

$$k_{mc} = (1 - \bar{f})^{-1} \tag{21}$$

where $\bar{f}$ is approximately the ratio of polymer molecules which have at least two contacts with another to those which have at least one contact. The $\bar{f}$ and k_{mc} values should of course be different for different homopolymers. Making the reasonable assumption that, for a copolymer,

$$\bar{f} = \left(\frac{\sigma_{2,a}}{\sigma_{2,a} + \sigma_{2,b}}\right)\bar{f}_a + \left(\frac{\sigma_{2,b}}{\sigma_{2,a} + \sigma_{2,b}}\right)\bar{f}_b \tag{22}$$

we obtain

$$k_{mc} = \frac{\sigma_{2a} + \sigma_{2b}}{\sigma_{2a}(1 - \bar{f}_a) + \sigma_{2b}(1 - \bar{f}_b)} \tag{23}$$

The shielding function, f_{sh}, and its limiting value at infinite dilution, k_{sh}, are related to the volume occupied by the polymer molecules. As a first approximation, let us assume for a copolymer

$$f_{sh} = \left(\frac{n_a v_a}{n_a v_a + n_b v_b}\right) f_{sh,a} + \left(\frac{n_b v_b}{n_a v_a + n_b v_b}\right) f_{sh,b} \tag{24}$$

and

$$k_{sh} = \left(\frac{n_a v_a}{n_a v_a + n_b v_b}\right) k_{sh,a} + \left(\frac{n_b v_b}{n_a v_a + n_b v_b}\right) k_{sh,b} \tag{25}$$

As has already been noted, the k_{sh} and f_{sh} functions for homopolymers (here designated $k_{sh,a}$, $f_{sh,a}$, etc.) depend on the molecular weights, intermolecular contact energies and temperature, presumably in a complicated way. It seems reasonable that these dependencies for copolymers having random mer distributions will conform approximately to the equations just given, but this needs to be tested.

The function m is related to k_{sh} and f_{sh} by eq. (9). From that equation and eqs. (24) and (25) we obtain

$$m = \frac{\ln\left[\dfrac{n_a v_a(1 - f_{sh,a}) + n_b v_b(1 - f_{sh,b})}{n_a v_a(1 - k_{sh,a}) + n_b v_b(1 - k_{sh,b})}\right]}{\ln V_1} \tag{26}$$

The contact energy constants in copolymer solutions can be assumed to vary with the relative surface areas for the two types of mers in accordance with the equations

$$\epsilon_{21} = \left(\frac{\sigma_{2,a}}{\sigma_{2,a} + \sigma_{2,b}}\right)\epsilon_{a1} + \left(\frac{\sigma_{2,b}}{\sigma_{2,a} + \sigma_{2,b}}\right)\epsilon_{b1} = \frac{\sigma_{2,a}\epsilon_{a1} + \sigma_{2,b}\epsilon_{b1}}{\sigma_{2,a} + \sigma_{2,b}} \tag{27}$$

and

$$\epsilon_{22} = \left(\frac{\sigma_{2,a}}{\sigma_{2,a} + \sigma_{2,b}}\right)^2 \epsilon_{aa} + \left(\frac{\sigma_{2,b}}{\sigma_{2,a} + \sigma_{2,b}}\right)^2 \epsilon_{bb} + 2\left(\frac{\sigma_{2,a}\sigma_{2,b}}{\sigma_{2,a} + \sigma_{2,b}}\right)\epsilon_{ab} \tag{28}$$

The ϵ's here are all energies per unit contact area, for contact between surfaces of the types specified by the subscripts. ϵ_{11} should of course be independent of the copolymer composition. Substitution into eq. (8) gives $\Delta\epsilon$ for the copolymer solution. Then, if k_σ is independent of the relative numbers of mers of the two types, W is given by eq. (6).

The average number of rigid segments per copolymer molecule is related to the corresponding numbers in the two types of homopolymer by the equation

$$n_r = k_{r,a}n_a + k_{r,b}n_b \tag{29}$$

where $k_{r,a}$ and $k_{r,b}$ are the ratios of the number of rigid segments to the number of mers, in the two homopolymers.

The restriction of orientational randomness at the flexible joints in the polymer chains should depend on the molecular surface areas of the polymer molecules and on an energetic factor, such as the function W expressing the preference for polymer–polymer contacts, rather than polymer–solvent contacts. The relative energetic factors affect the relative magnitudes of the orientation restriction constants ($k_{s,a}$, $k_{s,b}$) for different types of homopolymers. The magnitude of k_s for a copolymer solution can reasonably be related to these constants by the equation

$$k_s = \left(\frac{\sigma_{2,a}}{\sigma_{2,a} + \sigma_{2,b}}\right) k_{s,a} + \left(\frac{\sigma_{2,b}}{\sigma_{2,a} + \sigma_{2,b}}\right) k_{s,b} \tag{30}$$

Substitution of the equations given above into eqs. (3) and (10) gives equations relating the thermodynamic properties of solutions of copolymers to those of corresponding solutions of the component homopolymers. These resultant equations are quite complicated. Moreover, some of the assumed relationships are admittedly not much more than guesses, based on elementary (and often approximate) theoretical considerations. It is hoped, nevertheless, that they will be useful in guiding the further theoretical and experimental work needed to obtain better relationships.

The problem of dealing with solutions of block and graft copolymers is even more difficult than that of dealing with copolymer solutions in which the mers of the two types are randomly distributed. The equations deduced for the last-mentioned type should, however, serve as starting points for theoretical or experimental relationships for the other types. Although some guesses might be made as to the functions which would be expected to depend markedly on the distribution of the two kinds of mers in the polymer molecules and as to the direction of the effect, in each case, such speculations are probably unwarranted, until appropriate experimental data are available for testing them. Even for random copolymers, suitable experimental data for testing the theoretical relationships here presented are almost nonexistent.

The author hopes that the presentation of this theory at this time will, nevertheless, be useful in indicating the kinds of experimental data which will be most suitable for extension of our knowledge in this field.

References

1. For a brief treatment of this theory, with references, see M. L. Huggins, *Physical Chemistry of High Polymers*, Wiley, New York, 1958, Chap. 5.
2. Huggins, M. L., *J. Polymer Sci.*, **16**, 209 (1955); also ref. 1, Chap. 6.
3. Huggins, M. L., unpublished research.

Synopsis

Closed-form equations have been deduced for the partial molal energy and entropy of mixing for the solvent in a polymer solution, as functions of molecular and intermolecular properties. In the derivations the molecular interaction energies are computed per unit of molecular surface area. Allowance is made for both intramolecular and intermolecular contacts, also for blocking of access to interior segments of the polymer molecules. In the entropy equations, allowance is made for departure from perfect randomness resulting from different interaction energies between different types of molecular surface, and for the concentration dependence of the randomness of relative orientations of successive segments. Equations are presented for the pertinent molecular and intermolecular constants and other functions for a solution of a random copolymer, in terms of the corresponding constants and other functions for the related homopolymers. The theoretical treatment of nonrandom (block and graft) copolymers is briefly discussed.

Résumé

On a établi des équations concises pour l'énergie molaire partielle et l'entropie de mélange d'un solvant dans une solution polymérique, en fonction de propriétés moléculaires et intermoléculaires. Dans l'établissement de l'equation les énergies d'interaction moléculaire sont calculées par unité de surface moléculaire. On tient compte des contacts tant intramoléculaires qu'intermoléculaires, ainsi que de l'inaccessibilité aux segments internes des molécules de polymères. Dans les équations d'entropie, on tient compte d'écarts au hasard absolu, provenant de diverses interactions entre types différents de surfaces moléculaires; on tient aussi compte de la dépendance de la concentration, vis-à-vis de la probabilité des orientations relatives de segments successifs. Des équations sont présentées donnant des constantes moléculaires et intermoléculaires et d'autres équations pour une solution de copolymère statistique, exprimèes par les constantes correspondantes et autres fonctions des homopolyméres respectifs. On discute brièvement du développement théorique des polymères non-statistiques (en blocs et greffés).

Zusammenfassung

Für die partielle molare Mischungsenergie und -entropie für das Lösungsmittel in einer Polymerlösung als Funktion der molekularen und zwischenmolekularen Eigenschaften wurden Gleichungen in geschlossener Form abgeleitet. Bei der Ableitung wird die molekulare Wechselwirkungsenergie pro Flächeneinheit der Moleküloberfläche gerechnet. Intramolekulare und intermolekulare Kontakte und auch die Blockierung des Zuganges zu inneren Segmenten der Polymermoleküle werden berücksichtigt. Bei der Entropiebeziehung wird die Abweichung von der völlig ungeordneten Verteilung infolge verschiedener Wechselwirkungsenergien zwischen verschiedenen Moleküloberflächentypen und die Konzentrationsabhängigkeit des statistischen Charakters der relativen Orienterung aufeinanderfolgender Segmente in Rechnung gestellt. Gleichungen für die bezüglichen molekularen und intermolekularen Konstanten und andere Funktionen für eine Lösung eines statistischen Copolymeren werden in Beziehung zu den entsprechenden Konstanten und anderen Funktionen der betreffenden Homopolymeren angegeben. Die theoretische Behandlung nichtstatistischer (Block- und Pfropf-) Copolymerer wird Kurz diskutiert.

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Contribution a laThermodynamique des Solutions Très Diluées de Copolymères

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Dans des publications antérieures,[1,2] nous avons étudié les propriétés thermodynamiques des copolymères en solution en utilisant, pour évaluer l'entropie, la formule établie par Flory et Huggins pour un homopolymère. Cette évaluation s'est révélée trop grossière quand nous avons voulu passer à la deuxième approximation. Par la suite,[3] nous avons étendu aux copolymères la méthode quasi-chimique de Guggenheim. Cette approximation, basée comme on le sait, sur l'additivité des énergies d'interaction des paires de voisins premiers et sur l'indépendance statistique de ces paires, ne permet malheureusement pas de distinguer entre copolymères "statistiques" et "greffés" (ou blocs). Elle ne tient pas compte de la disposition différente des séquences des constituants dans ces deux types de copolymères. Or il est évident intuitivement que la place relative des segments de nature chimique différente qui composent le copolymère influe sur le nombre de configurations que peuvent prendre les chaînes en solution et, par conséquent, sur l'entropie (sauf dans le cas des solvants communs parfaits).

1. MODÈLE ET MODE DE REPRÉSENTATION

Nous avons donc étudié sur un modèle simple le sens de variation du nombre des configurations les plus probables d'une chaîne de copolymère avec la place relative des constituants A et B dans la chaîne. Une chaîne isolée de copolymère est placée dans toutes les configurations possibles sur un réseau quasicristallin à deux dimensions (nombre de coordination $z = 4$). Chaque segment de la chaîne occupe un noeud du réseau, les autres noeuds étant remplis par les molécules du solvant. Notre modèle nous limite donc au cas des solutions très diluées où il n'y a pas interaction entre les différentes chaînes ($nN_p \ll N_0$), n étant le nombre moyen de segment dans la chaîne, N_p le nombre de chaînes en solution, N_0 le nombre de molécules du solvant).

Une méthode analogue a été utilisée par Orr[4] pour le cas d'un homopolymère jusqu'à $n = 9$. Nous avons poussé ce cas jusqu'à $n = 10$ (2018. figurations). Pour les 9 premières valeurs de n, nos résultats concordent exactement avec ceux de Orr (Fig. 1).

Nous avons dessiné les configurations pour les types de copolymères sui-

vants: copolymère composé de segments A et B régulièrement alternés, que nous désignerons par $(AB)_n$; copolymère constitué de deux séquences de longueur égale de segments A et B, que nous appellerons A_nB_n.

Pour chaque cas, nous avons fait plusieurs hypothèses. (*1*) A et B sont

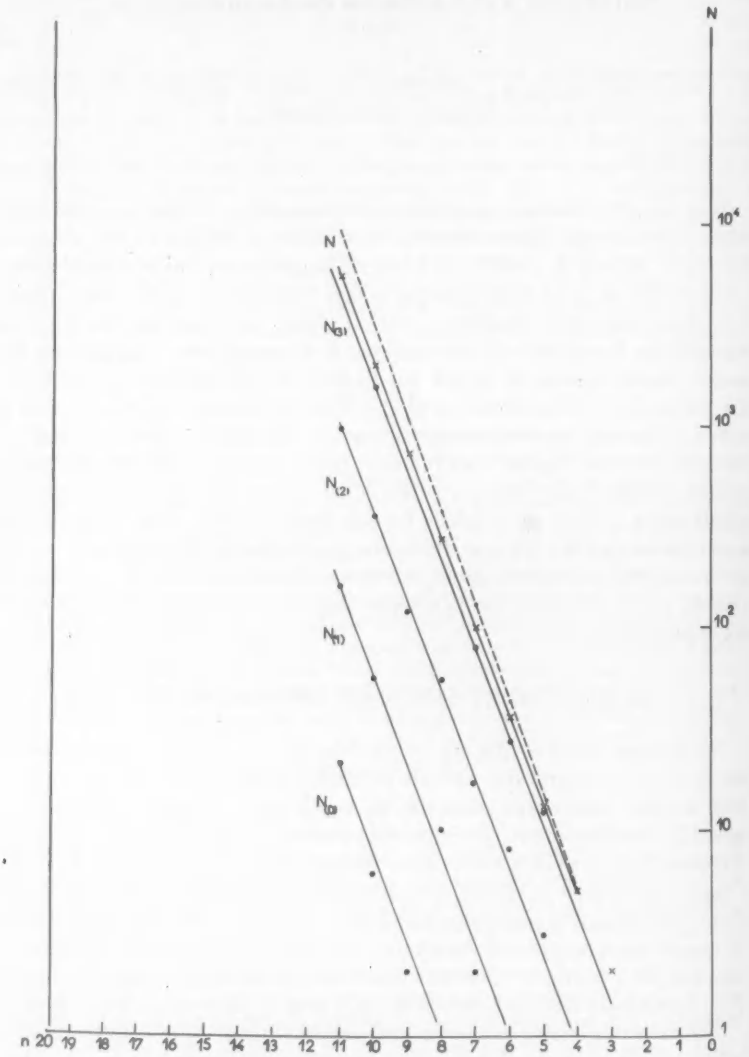

Fig. 1. Homopolymere soluble. La droite en pointillé correspond a la formule $N = [(z-1)^{n-2} + 1]/2$, qui donne le nombre de configurations distinctes si l'on ne tient pas compte des places déjá occupées par la chaine sur le réseau. En utilisant cette formule on ferait une erreur d'environ 30% sur le nombre de configurations.

tous deux solubles: (*a*) A et B sont compatibles en solution; (*b*) A et B sont incompatibles en solution. (*2*) A est soluble, B est insoluble: (*a*) A et B sont compatibles; (*b*) A et B sont incompatibles.

Comment figurer sur le réseau plan ces diverses propriétés?

Supposons déjà placés sur le réseau n segments d'une chaîne; si le polymère est soluble, le $(n + 1)^e$ segment se placera indifféremment sur les $(z - 1) = 3$ places libres en bout de chaîne sur le réseau; s'il est mal soluble, le $(n + 1)^e$ segment aura tendance à se rapprocher d'un segment de même nature et se placera préférentiellement sur une ou deux des trois places possibles.

Si A et B sont compatibles, nous leur permettront d'être voisins premiers sur le réseau (lorsque A et B sont tous deux solubles, ce cas se confond dans notre modèle avec celui de l'homopolymère soluble).

Si A et B sont incompatibles, ils ne pourront être voisins premiers ou même voisins seconds, suivant leur degré d'incompatibilité.

L'examen du Tableau I, où sont représentées les configurations pour de courtes longueurs de chaînes, permettra de mieux comprendre le mécanisme de la représentation.

Pour le cas 1, $n = 4$, il y a 9 configurations dont 4 sont distinctes. Parmi ces 4 configurations: 3 donneront $(z - 1) = 3$ configurations pour $n = 5$; 1 donnera $(z - 2) = 2$ configurations pour $n = 5$ (1 place déjà occupée par la chaîne). N.B.: la configuration linéaire de $n = 4$ doit en réalité être comptée comme une chaîne donnant seulement 2 configurations puisque, parmi les 3 configurations qu'elle donne pour $n = 5$, 2 sont symétriques.

Pour le cas 2, $n = 4$, il y a 7 configurations, 4 distinctes: 2 donneront $(z - 1) = 3$ configurations pour $n = 5$; 2 donneront $(z - 2) = 2$ configurations pour $n = 5$ (A et B ne peuvent être voisins premiers). N.B.: ici encore, la configuration linéaire sera considérée comme donnant seulement 2 configurations pour $n = 5$, 2 parmi les 3 configurations qu'elle fournit étant symétriques.

Pour le cas 3, $n = 4$, il y a 4 configurations dont 2 sont distinctes. Chacune de ces 2 chaînes donnera 2 configurations pour $n = 5$ (A et B ne peuvent être voisins premiers).

Pour le cas 4, $n = 4$, il y a 7 configurations dont 4 distinctes. Parmi ces 4 configurations: 2 donneront $(z - 1)(z - 2) = 6$ configurations pour $n = 6$; 1 donnera $(z - 2)(z - 2) = 4$ configurations pour $n = 6$; 1 donnera $(z - 1)^2 = 9$ configurations pour $n = 6$. Mais cette dernière est la configuration linéaire de $n = 4$ qui donne, pour $n = 6$, 5 configurations distinctes seulement. On a donc 21 configurations distinctes pour $n = 6$.

Pour le cas 5, $n = 4$, il y a 1 seule configuration (A et B ne peuvent être voisins seconds). Pour $n = 6$, il y a 9 configurations dont 5 sont distinctes. Parmi celles-ci: 2 donneront $(z - 1)(z - 2) = 6$ configurations pour $n = 6$; 2 donneront $(z - 2)(z - 2) = 4$ configurations pour $n = 6$; 1 donnera $(z - 1)^2 = 9$ configurations pour $n = 6$. Cette dernière configuration est la configuration linéaire qui, pour $n = 6$, donne seulement 5 configurations distinctes. On a donc en tout 25 configurations distinctes pour $n = 6$.

vants: copolymère composé de segments A et B régulièrement alternés, que nous désignerons par $(AB)_n$; copolymère constitué de deux séquences de longueur égale de segments A et B, que nous appellerons A_nB_n.

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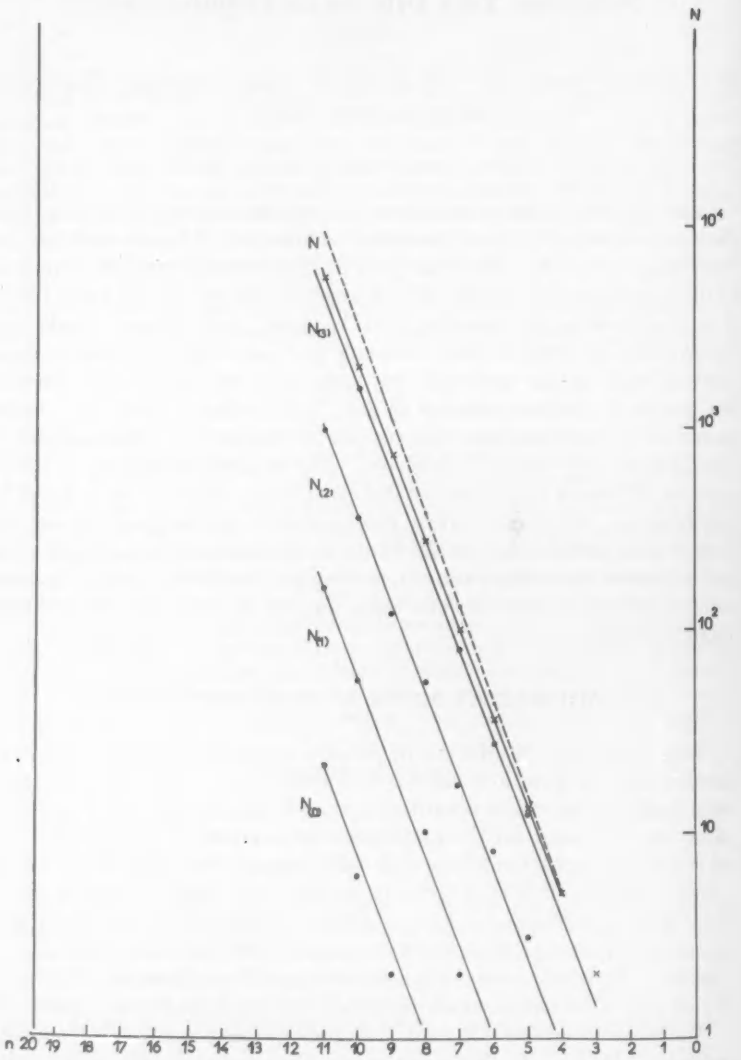

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L'examen du Tableau I, où sont représentées les configurations pour de courtes longueurs de chaînes, permettra de mieux comprendre le mécanisme de la représentation.

Pour le cas 1, $n = 4$, il y a 9 configurations dont 4 sont distinctes. Parmi ces 4 configurations: 3 donneront $(z - 1) = 3$ configurations pour $n = 5$; 1 donnera $(z - 2) = 2$ configurations pour $n = 5$ (1 place déjà occupée par la chaîne). N.B.: la configuration linéaire de $n = 4$ doit en réalité être comptée comme une chaîne donnant seulement 2 configurations puisque, parmi les 3 configurations qu'elle donne pour $n = 5$, 2 sont symétriques.

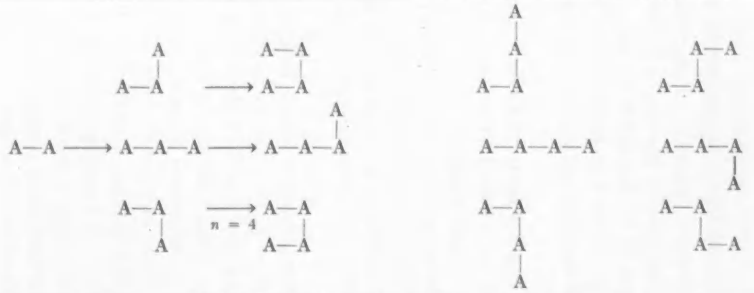
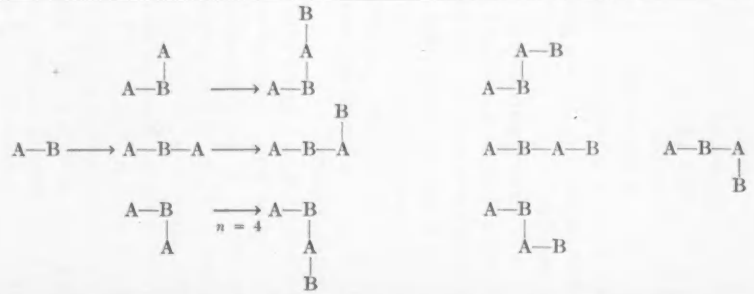
Pour le cas 2, $n = 4$, il y a 7 configurations, 4 distinctes: 2 donneront $(z - 1) = 3$ configurations pour $n = 5$; 2 donneront $(z - 2) = 2$ configurations pour $n = 5$ (A et B ne peuvent être voisins premiers). N.B.: ici encore, la configuration linéaire sera considérée comme donnant seulement 2 configurations pour $n = 5$, 2 parmi les 3 configurations qu'elle fournit étant symétriques.

Pour le cas 3, $n = 4$, il y a 4 configurations dont 2 sont distinctes. Chacune de ces 2 chaînes donnera 2 configurations pour $n = 5$ (A et B ne peuvent être voisins premiers).

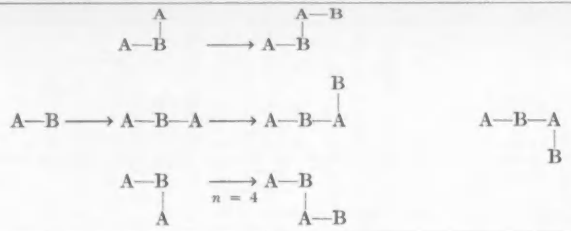
Pour le cas 4, $n = 4$, il y a 7 configurations dont 4 distinctes. Parmi ces 4 configurations: 2 donneront $(z - 1)(z - 2) = 6$ configurations pour $n = 6$; 1 donnera $(z - 2)(z - 2) = 4$ configurations pour $n = 6$; 1 donnera $(z - 1)^2 = 9$ configurations pour $n = 6$. Mais cette dernière est la configuration linéaire de $n = 4$ qui donne, pour $n = 6$, 5 configurations distinctes seulement. On a donc 21 configurations distinctes pour $n = 6$.

Pour le cas 5, $n = 4$, il y a 1 seule configuration (A et B ne peuvent être voisins seconds). Pour $n = 6$, il y a 9 configurations dont 5 sont distinctes. Parmi celles-ci: 2 donneront $(z - 1)(z - 2) = 6$ configurations pour $n = 6$; 2 donneront $(z - 2)(z - 2) = 4$ configurations pour $n = 6$; 1 donnera $(z - 1)^2 = 9$ configurations pour $n = 6$. Cette dernière configuration est la configuration linéaire qui, pour $n = 6$, donne seulement 5 configurations distinctes. On a donc en tout 25 configurations distinctes pour $n = 6$.

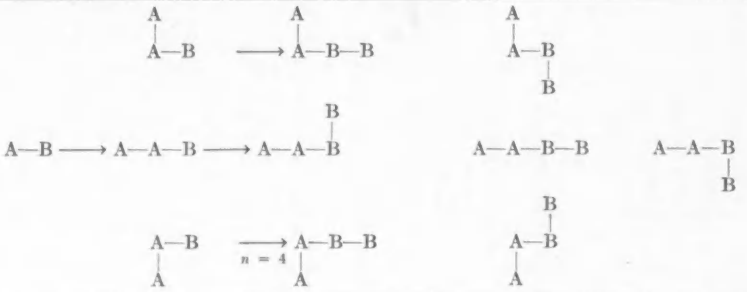
TABLEAU I

Cas no	Type de polymère	Configurations
(1)	Homopolymère soluble	
(2)	Copolymère alterné $(AB)_n$, A et B solubles; ils ne peuvent être voisins premiers	

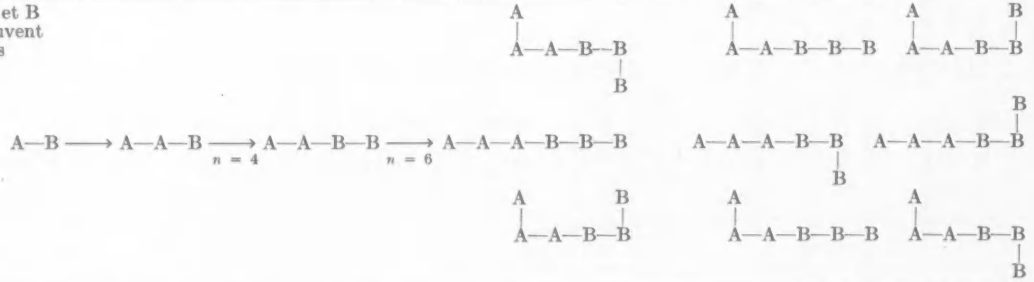
(3) Copolymère alterné $(AB)_n$, A soluble, B insoluble; A et B ne peuvent être voisins premiers



(4) Copolymère A_nB_n, A et B solubles; ils ne peuvent être voisins premiers

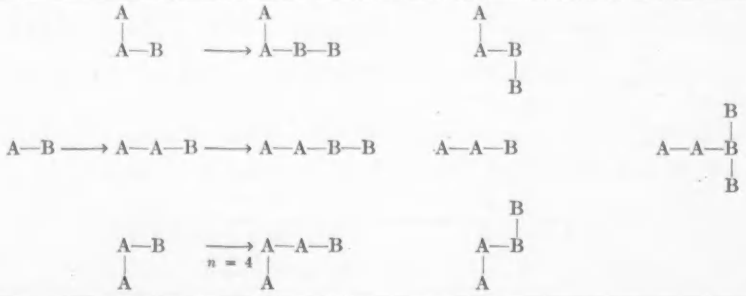
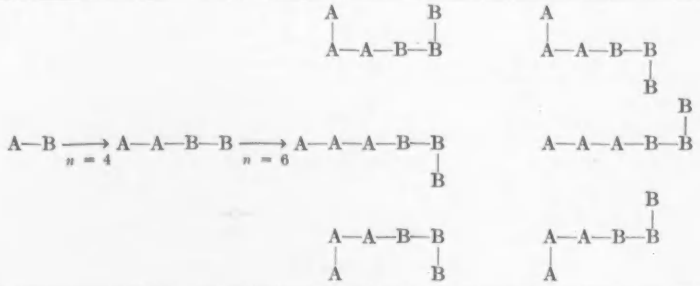
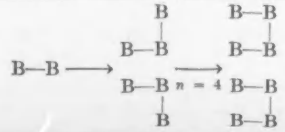


(5) Copolymère A_nB_n, A et B solubles; ils ne peuvent être voisins seconds



(continued)

TABLEAU I (*continued*)

Cas no	Type de polymère	Configurations
(6)	Copolymère A_nB_n, A soluble, B insoluble; A et B ne peuvent être voisins premiers	
(7)	Copolymère A_nB_n, A soluble, B insoluble; A et B ne peuvent être voisins seconds	
(8)	Homopolymère insoluble	

Pour le cas 6, $n = 4$, il y a 7 configurations dont 4 sont distinctes. Parmi celles-ci: 1 donnera $(z - 2)(z - 2) = 4$ configurations pour $n = 6$; 1 donnera $(z - 2)(z - 3) = 2$ configurations pour $n = 6$; 1 donnera $(z - 1)(z - 3) = 3$ configurations pour $n = 6$; 1 donnera $(z - 1)(z - 2) = 6$ configurations pour $n = 6$, dont 3 seulement sont distinctes. On aura donc au total 12 configurations distinctes pour $n = 6$.

Pour le cas 7, $n = 6$, il y a 6 configurations dont 3 sont distinctes: 2 donneront $(z - 2)(z - 3) = 2$ configurations pour $n = 8$; 1 donnera $(z - 1)(z - 3) = 3$ configurations pour $n = 8$. Au total, il y a 7 configurations distinctes pour $n = 8$.

Pour le cas 8, $n = 4$, 1 seule configuration (2 configurations symétriques).

2. RÉSULTATS

Si l'on porte le logarithme du nombre de configurations N pour une longueur de chaîne n donnée en fonction de n, on obtient une droite après quelques fluctuations pour les très courtes longueurs de chaîne. Ceci est vrai pour tous les cas étudiés sauf pour l'homopolymère insoluble (Figs. 1-4).

Nous avons vérifié la linéarité de log N pour des configurations de longueur double de celle que nous avons dessinées, en portant avec un calque des chaînes de longueur n choisies au hasard dans toutes les positions possibles à l'extrêmité de chaînes de longueur n également choisies au hasard. En calculant le nombre moyen de configurations données pour $2n$ par un grand nombre de chaînes de n, nous avons trouvé un point qui se plaçait sur la droite log N.

Dans les tableaux II–VIII, nous avons tracé un trait double pour indiquer jusqu'à quelle valeur de n nous avons effectivement dessiné les configurations.

TABLEAU II[a]

Homopolymère Soluble

$\text{Log } N = 0{,}43854n - 1{,}07850$; $N_T = 4(2N - 1)$

n	N	$N_{(3)}$	$N_{(2)}$	$N_{(1)}$	$N_{(0)}$
1					
2	1				
3	2				
4	4				
5	10	10	3		
6	36	27	8	1	
7	98	79	17	2	
8	273	207	55	10	1
9	740				
10	2018	1596	360	56	6
11	5565	4391	990	163	21

[a] Nous avons dénombré les configurations distinctes. La configuration linéaire de n qui pour $n + 1$ donne 3 configurations dont 2 seulement sont distinctes a été comptée dans les $N_{(2)}$.

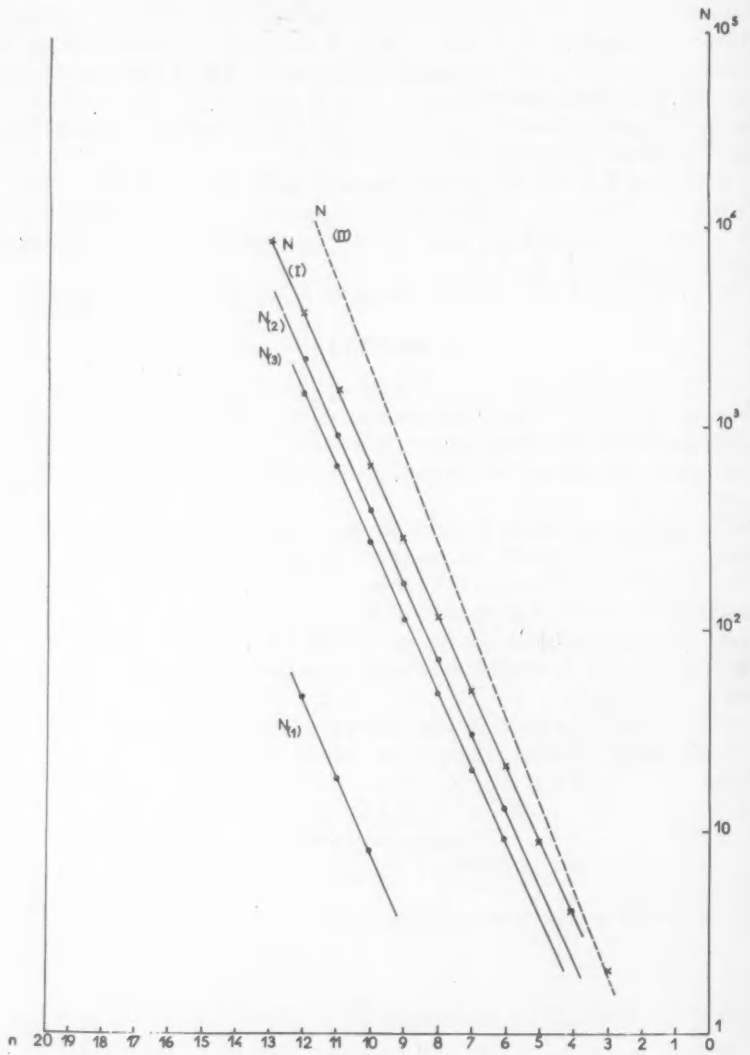


Fig. 2. Copolymere $(AB)_n$: (*I*) A et B sont solubles, ils ne peuvent être voisin premiers; (*II*) Nombre de configurations lorsque A et B peuvent être voisins premiers elle se confond avec la courbe de l'homopolymère soluble.

Pour l'homopolymère et les copolymères de type $(AB)_n$, nous avons aussi dénombré le nombre de configurations d'une chaîne de longueur n qui donneront pour $n + 1$ respectivement $(z - 1) = 3$, $(z - 2) = 2$, $(z - 3) = 1$ et $(z - 4) = 0$ configurations. Ces nombres, que nous désignerons par

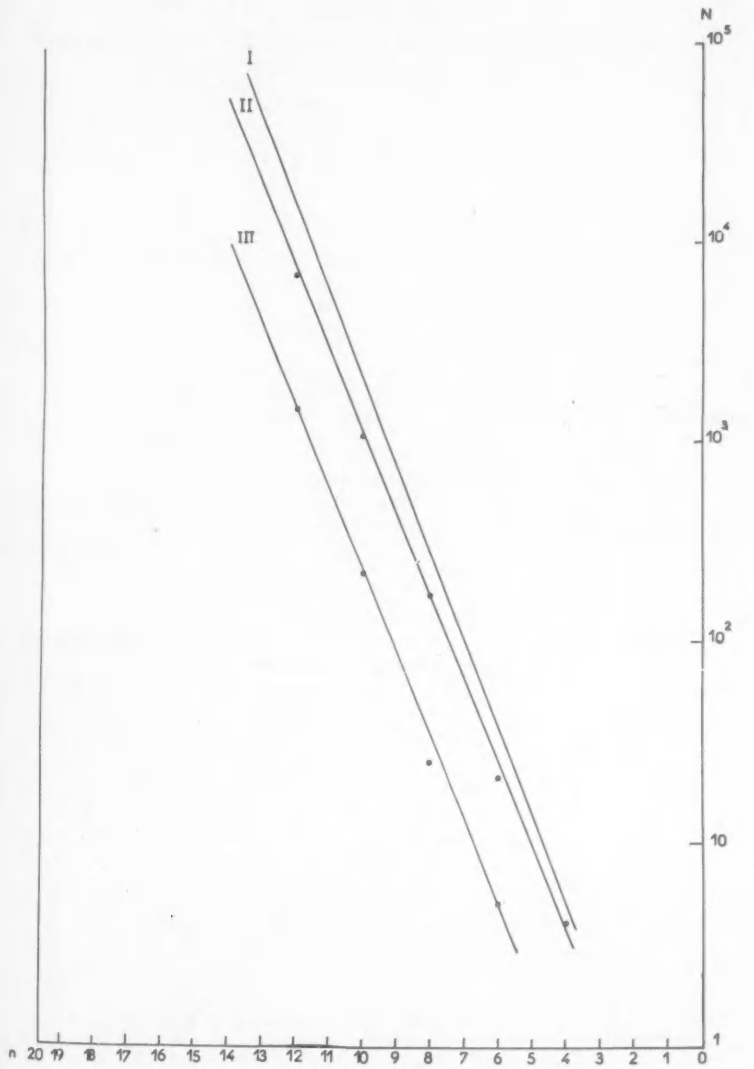


Fig. 3. Copolymère AnBn, A et B sont solubles: (*I*) A et B peuvent être voisins premiers (identique au cas de l'homopolymere dans notre modèle); (*II*) A et B ne peuvent être voisins premiers; (*III*) A et B ne peuvet être voisins seconds.

$N_{(3)}$, $N_{(2)}$, $N_{(1)}$ et $N_{(0)}$, sont également portés dans les Tableaux II, III et IV. Pour les copolymères de type A_nB_n que nous avons fait croitre par les deux extrêmités (Tableaux V–VIII), nous avons dénombré: $N_{(9)}$, $N_{(8)}$, $N_{(7)}$,

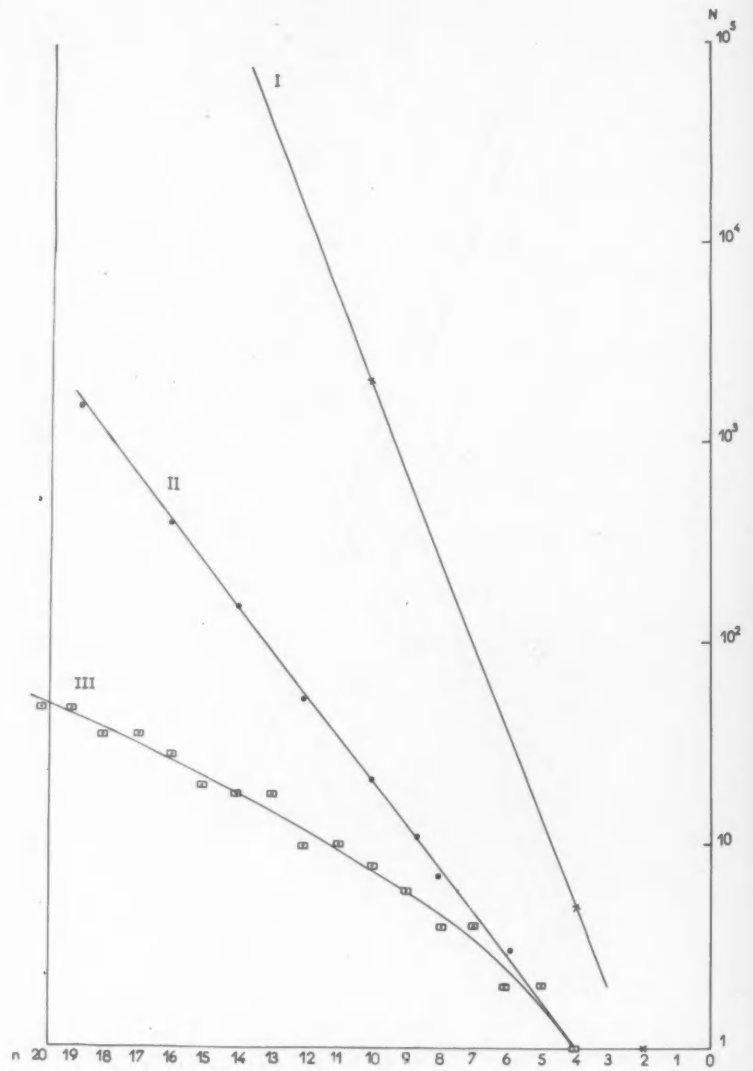


Fig. 4. Copolymere AnBn, A soluble, B insoluble; (*I*) homopolymère soluble; (*II*) A et B ne peuvent être voisins seconds; (*III*) homopolymère insoluble. Si on appelle $\gamma = \phi A/\phi B$ la composition en volume du copolymère, $\gamma = 0{,}5$ correspond a la courbe *II*. Lorsque γ tendra vers 1, la courbe de variation de N tendra vers la courbe (*I*); quant γ tendra vers 0, la courbe de variation se rapprochera de *III*.

TABLEAU III[a]

Copolymère $(AB)_n$, A et B Solubles; A et B ne Peuvent Être Voisins Premiers[b]
Log $N = 0{,}3670n - 0{,}840$; $N_T = 4(2N - 1)$

n	N	$N_{(3)}$	$N_{(2)}$	$N_{(1)}$	$N_{(0)}$
1					
2	1				
3	2				
4	4				
5	9				
6	21	8	13		
7	50	19	30	1	
8	118	47	70	1	
9	282	112	167	3	
10	673	273	389	8	
11	1605	660	927	18	
12	3852	1525	2280	47	
13	9182				

[a] La configuration linéaire pour n donné a été comptée dans les $N_{(2)}$ et pas dans les $N_{(3)}$ car elle donne 3 configurations dont 2 seulement sont distinctes.

[b] Ce cas ne se distingue pas dans notre modèle de celui ou A et B ne peuvent être voisins seconds.

TABLEAU IV[a]

Copolymère $(AB)_n$, A Soluble, B Insoluble; A et B ne Peuvent Etre Voisins Premiers
Log $N = 0{,}22543n - 0{,}60335$; $N_T = 8N$

n	N	$N_{(3)}$	$N_{(2)}$	$N_{(1)}$	$N_{(0)}$
2	1	0			
3	2	0			
4	2	0			
5	4	0	2	2	0
6	6	0			
7	12	0	5	7	0
8	17	0	15	2	0
9	32	0	14	18	0
10	46	0	44	2	0
11	90	0	38	51	1
12	127	0	123	4	0
13	250	0	109	139	2
14	357	0	342	14	1
15	698	0	311	385	2
16	1007	0	964	32	11
17	1960	0	893	1061	6
18	2847	0			

[a] Avec notre modèle, ce cas ne se distingue pas de celui où A et B ne peuvent être voisins seconds (à cause de l'alternance régulière de A et B). Les valeurs de N qui nous intéressent sont celles qui correspondent à n pair.

TABLEAU V

Copolymère A_nB_n, A et B Solubles; A et B ne Peuvent Être Voisins Premiers
Log $N = 0{,}40621n - 1{,}02868$; $N_T = 4(2N - 1)$

n	N	$N_{(0)}$	$N_{(1)}$	$N_{(2)}$	$N_{(3)}$	$N_{(4)}$	$N_{(5)}$	$N_{(6)}$	$N_{(7)}$	$N_{(8)}$	$N_{(9)}$
2	1										
4	4					1	1	2			
6	21						3	2			16
8	171		1	5	25	4	3	40	0	4	89
10	1080		3	40	180	20	16	379	2	20	420
12	7011										

TABLEAU VI[a]

Copolymère A_nB_n, A et B Solubles; A et B ne Peuvent Être Voisins Seconds
Log $N = 0{,}406795n - 1{,}70952$; $N_T = 4(2N - 1)$

n	N	$N_{(\ )}$	$N_{(1)}$	$N_{(2)}$	$N_{(3)}$	$N_{(4)}$	$N_{(5)}$	$N_{(6)}$	$N_{(7)}$	$N_{(8)}$	$N_{(9)}$
2											
4	1										
6	5										
8	25						1			1	23
10	220		4	10	33	4	2	54		0	113
12	1486		8	86	252	72	2	350		9	707
14	9674										

[a] Nous avons dénombré les configurations distinctes. Pour n donné, la configuration linéaire qui pour $n + 2$ donne 9 configurations dont 5 seulement sont distinctes doit être comptée comme une $N_{(5)}$ et non comme une $N_{(9)}$.

$N_{(6)}$, $N_{(5)}$, $N_{(4)}$, $N_{(3)}$, $N_{(2)}$, $N_{(1)}$, $N_{(0)}$, qui sont le nombre de configurations de chaînes de longueur n qui, pour $n + 2$, donnent respectivement:

$(z - 1)^2 = 9$ configurations

$(z - 1)^2 - 1 = 8$ configurations

$(z - 1)^2 - 2 = 7$ configurations

$(z - 1)(z - 2) = 6$ configurations

$(z - 1)(z - 2) - 1 = 5$ configurations

$(z - 2)(z - 2) = 4$ configurations

$(z - 4) + (z - 1)$ ou $(z - 1)(z - 3) = 3$ configurations

$(z - 4) + (z - 2)$ ou $(z - 1)(z - 3) - 1 = 2$ configurations

$(z - 4) + (z - 3)$ ou $(z - 3)(z - 3) = 1$ configurations

Le dépouillement de ces $N_{(i)}$ permet en effet de calculer le nombre de configurations pour $n + 1$ dans le cas $(AB)_n$ ou pour $n + 2$ dans le cas A_nB_n à partir des configurations dessinées pour n lorsque le nombre de ces configurations devient trop élevé pour être matérialisé. Il y a d'autre

TABLEAU VII

Copolymère A_nB_n, A Soluble, B Insoluble; A et B Peuvent Être Voisins Seconds
Log $N = 0{,}24986n - 0{,}38792$; $N_T = 8N$ à partir de $n = 6$

n	N	$N_{(1)}$	$N_{(2)}$	$N_{(3)}$	$N_{(4)}$	$N_{(5)}$	$N_{(6)}$
2	1				1		
4	4	0	1	2	1		
6	12		1	11			
8	34	2	5	15	1		11
10	127	3	19	91	1		13
12	396	8	39	299	7	1	42
14	1268	26	160	930	24	2	126
16	3998						

TABLEAU VIII

Copolymère A_nB_n, A Soluble, B Insoluble; A et B ne Peuvent Être Voisins Seconds
Log $N = 0{,}22125n - 0{,}91942$; $N_T = 8N$

n	N
2	1
4	1
6	3
8	7
10	21
12	53
14	155
16	410

part une relation entre les $N_{(i)}$ et le nombre de couples de voisins proches et seconds de diverses natures (AA, BB ou AB) et leur dénombrement pourra nous servir pour une approximation ultérieure. Les courbes de variations des $N_{(i)}$ en fonction de n sont des droites parallèles à log N. Nous avons étudié plus particulièrement la variation des $N_{(i)}$ pour le cas de l'homopolymère soluble. En attribuant à log $N_{(i)}$ le même coefficient angulaire qu'à log N et une ordonnée à l'origine obtenue en faisant la moyenne sur les points "expérimentaux," on est conduit à attribuer à chacune des droites les équations suivantes:

$$\log N_{(3)} = 0{,}43854n - 1{,}18138$$
$$\log N_{(2)} = 0{,}43854n - 1{,}8283$$
$$\log N_{(1)} = 0{,}43854n - 2{,}61175$$
$$\log N_{(0)} = 0{,}43854n - 3{,}50172$$

Pour $n = 11$, on trouve alors:

$$N_{(3)} = 4391$$
$$N_{(2)} = 990$$
$$N_{(1)} = 163$$
$$N_{(0)} = 21$$

et

$$N = N_{(3)} + N_{(2)} + N_{(2)} + N_{(0)} = 5565$$

En calculant N pour $n = 11$ à partir de l'équation de la droite $\log (N) = f(n)$, on trouve 5 563.
Pour $n = 100$:

$$N_{(3)} = 4705 \times 10^{39}$$
$$N_{(2)} = 1061 \times 10^{39}$$
$$N_{(1)} = 175 \times 10^{39}$$
$$N_{(0)} = 22 \times 10^{39}$$
$$N = 5963 \times 10^{49}$$

Orr[4] a dépouillé pour une longueur de chaîne donnée le nombre de contacts premiers entre deux segments d'homopolymère. Si on porte le nombre de configurations ayant 1, 2, 3, ..., contacts en fonction de n, on trouve avec ses données des courbes qui coupent la droite du nombre total des configurations. C'est évidemment impossible. Il doit donc y avoir une erreur dans le dépouillement de Orr. En le reprenant pour le matériel statistique que nous possédons jusqu'à $n = 10$, nous trouverions vraisemblablement des droites parallèles à $\log N$, ce qui permettrait des extrapolations fournissant par soustraction de proche en proche le nombre de chaînes ayant 1, 2, 3, 4, ..., p contacts pour n quelconque, à partir des valeurs trouvées jusqu'à $n = 10$. On pourrait ainsi déterminer l'énergie des différentes configurations et leur poids statistique, ce qui conduirait à la fonction de partition du système. C'est la deuxième approximation dont nous parlions plus haut. Dans notre cas, il faudra de plus tenir compte des contacts seconds AA et BB, car c'est indispensable pour obtenir une différence dans le nombre de configurations pour les types $(AB)_n$ et A_nB_n.

3. EVALUATION DE L'ENTROPIE

Nous admettrons que, pour chaque type de copolymère, l'énergie E du système chaîne-solvant est la même en première approximation pour toutes les configurations possibles de la chaîne. L'entropie de mélange sera alors:

$$\Delta S = (R/n)(\ln N - \ln N_p - \ln N_S) \qquad (1)$$

avec: R = constante des gaz, N = nombre de configurations d'une chaîne de longueur donnée en solution, N_p = nombre de configurations de la chaîne précipitée. Il sera le même pour tous les types de chaînes, les contacts "interdits" en solution ne l'étant plus. Ce nombre varie en fonction de n, pour $n > 20$, suivant la relation

$$\log N_p = 0{,}0669n + 0.372$$

Pour $n = 100$,

$$(R/n) \ln N_p = 0{,}3248 \text{ (calculé par mole de segments)}$$

N_S = nombre de configurations du solvant pur lorsque les molécules occupent tous les noeuds du réseau $N_S = 1$ et $\ln N_S = 0$.

La formule (1) devient alors

$$\Delta S = (R/n)(\ln N - 0{,}32) \qquad (2)$$

Les valeurs de ΔS exprimées en moles de segments sont portées dans le Tableau IX pour $n = 100$.

TABLEAU IX

Cas	Type de la chaîne	ΔS
1	Homopolymère soluble	1,65
2	Copolymère $(AB)_n$, A soluble, B soluble; A et B ne peuvent être voisins premiers	1,33
3	Copolymères $(AB)_n$, A soluble, B insoluble; A et B ne peuvent être voisins premiers	0,69
4	Copolymère A_nB_n, A soluble, B soluble; A et B ne peuvent être voisins premiers	1,50
5	Copolymère A_nB_n, A soluble, B soluble; A et B ne peuvent être voisins seconds	1,47
6	Copolymère A_nB_n, A soluble, B insoluble; A et B ne peuvent être voisins premiers	0,81
7	Copolymère A_nB_n, A soluble, B insoluble; A et B ne peuvent être voisins seconds	0,66

On voit en comparant (2) avec (4) et (3) avec (6) qu'à compositions qualitative et quantitative égales, le copolymère de structure A_nB_n est plus soluble que le copolymère de type $(AB)_n$.

La comparaison de (4) et (5), montre que lorsque A et B sont tous deux solubles, il n'y a pratiquement pas de différence que A et B puissent être voisins seconds ou non.

Quand B est insoluble, la différence est plus importante La solubilité du copolymère A_nB_n diminue lorsque l'incompatibilité des constituants augmente.

Ecartement des Extrémités des Chaînes

Nous avons profité du matériel accumulé pour faire la statistique des écartements des extrémités des configurations, qui peuvent donner des indications sur les viscosités des solutions.

Pour $n = 10$, nous avons l'ensemble des configurations pour tous les cas étudiés. Le Tableau X indique le résultat des mesures.

Les copolymères de type A_nB_n ont le maximum apparent de la courbe situé au même endroit que l'homopolymère soluble (Figs. 5). Mais la densité des grands écartements est plus forte que pour l'homopolymère et augmente avec le degré d'incompatibilité des constituants. Ceci est

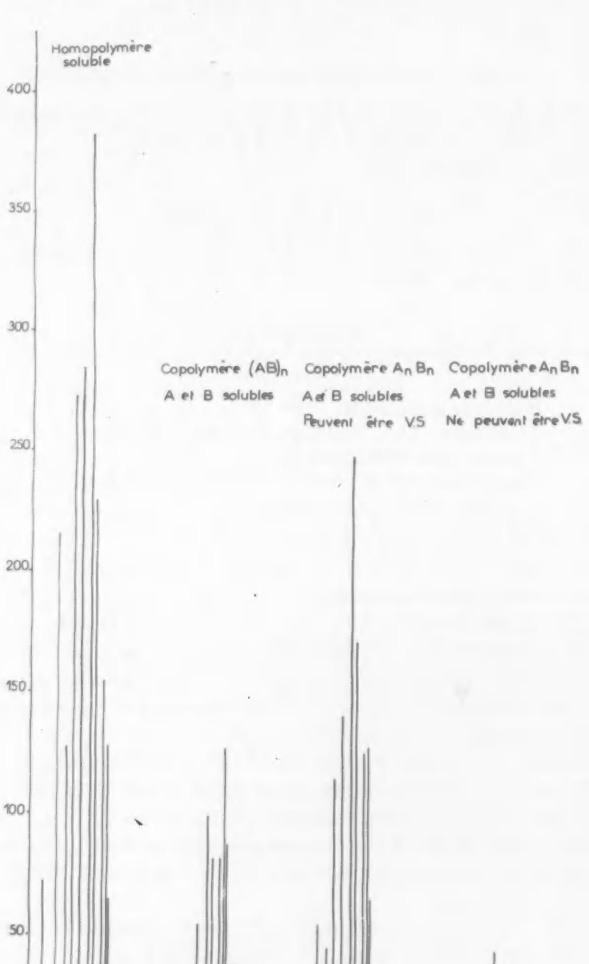


Figure 5.

normal puisque les contacs "interdits" sont plus fréquents dans les chaines les plus repliées sur elles-mêmes.

Le maximum apparent des copolymères $(AB)_n$ se trouve à 3,2 alors que celui de l'homopolymère soluble est à 2,5. La fréquence des grands écartements diminue lorsque B devient insoluble comme on devait s'y attendre.

TABLEAU X

Cas	Type du Polymère	Position du maximum pour $n = 10$	Hauteur du maximum pour $n = 10$	Nombre de configuration pour $n = 10$	Position du maximum pour $n = 20$
1	Homopolymère soluble	2,5	380	2018	4
2	Copolymère $(AB)_n$, A et B solubles; A et B ne peuvent être voisins premiers	3,2	126	673	5
3	Copolymère A_nB_n, A et B solubles; A et B ne peuvent être voisins premiers	2,5	247	1080	4
4	Copolymère A_nB_n, A et B solubles; A et B ne peuvent être voisins seconds	2,5	44	220	4
5	Copolymère $(AB)_n$, A soluble, B insoluble; A et B ne peuvent être voisins premiers	3,2	17	46	5
6	Copolymère A_nB_n, A soluble, B insoluble; A et B ne peuvent être voisins premiers	2,5	36	127	4
7	Copolymère A_nB_n, A soluble, B insoluble; A et B ne peuvent être voisins seconds	2,5	10	41	4

Si l'on compare les copolymères A_nB_n et $(AB)_n$ dans le cas où A et B sont solubles et peuvent être voisins seconds, le maximum se situe pour le premier à 2,5 pour le second à 3,2. La densité des petits écartements est plus forte chez $(AB)_n$ que chez A_nB_n.

Nous avons également fait des statistiques pour $n = 20$ en portant avec des calques des configurations de $n = 10$ choisies au hasard à l'extrémité d'autres configurations de $n = 10$ également choisies au hasard. Les résultats sont portés dans la dernière colonne du Tableau X (les mesures portaient en moyenne sur 1000 configurations par type de copolymère). On peut faire les mêmes remarques que pour $n = 10$. Pour $n = 10$, il semble y avoir deux maximas secondaires entourant le maximum principal. Sur les statistiques pour $n = 20$, on voit également se dessiner trois distributions mais les lots de configurations étudiés sont très faibles par rapport à la population totale. Il est donc difficile de conclure à leur existence.

Références

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Résumé

L'expérience montre que les copolymères "statistiques" et "blocs" en solution présentent des propriétés thermodynamiques différentes, à composition identique. Les

théories classiques de solubilité ne permettent pas de prévoir ces différences de comporte ment. Nous avons essayé d'y parvenir en évaluant le sens de variation de l'entropie avec la nature du copolymère, en dessinant effectivement dans chaque cas, sur un réseau plan, les diverses configurations que peut prendre une chaîne de longueur donnée. Nous avons tenu compte des énergies d'inter-action des voisins premiers et seconds. Ce modèle nous limite au cas des solutions très diluées, où il n'y a pas interaction entre deux chaînes. Lorsqu'il devenait matériellement impossible de représenter les diverses configurations (au dessus de 3000 environ), nous avons effectué des statistiques sur des populations de chaînes de longueur n, construites au hasard à partir des chaînes de longueur $n/2$. Nous évaluons également le sens de variation des écartements des extremités des chaînes avec la nature du copolymère et les propriétés des constituants. Une tentative est faite pour généraliser à un réseau de nombre de coordination quelconque et établir une relation donnant le nombre de configurations d'une chaîne de longueur n, en fonction de n.

Synopsis

Experiments show that conventional and block copolymers of the same composition show in solutions different thermodynamic properties. Classical theories of the solubility are unable to predict these differences of behaviour. An attempt was made by evaluating the sign of the variation of entropy with the nature of the copolymer, by drawing effectively in each case on a plane the various possible configurations of a chain of a given length. Interaction energies between the first and the second neighbors have been taken into account. This model must be restricted to very dilute solutions, where interaction between different chains may be neglected. When it becomes practically impossible to represent the various configurations (above about 3000) statistics were used of the population of chains with length n, builded up statistically from chains with length $n/2$. The sign of the variation of the mean square distance between chain ends was also evaluated in function of the nature of the copolymer and the properties of the constituents. An attempt was made for generalizing it to a network with undetermined coordination number, and for establishing a relation between the number of configuration of a chain with n unities and this same number n.

Zusammenfassung

Die Erfahrung lehrt, dass "statistische" und "Block"-Copolymere bei identischer Zusammensetzung in Lösung verschiedene thermodynamische Eigenschaften aufweisen. Die klassischen Löslichkeitstheorien lassen keine solchen Unterschiede erwarten. Um entsprechende Angaben machen zu können wurde die Abhängigkeit der Entropie von der Natur des Copolymeren bestimmt. Für jeden Fall wurden in ein ebenes Netz die verschiedenen für eine Kette von gegebener Länge möglichen Konfigurationen eingetragen. Die Wechselwirkungsenergien mit nächsten und zweitnächsten Nachbarn wurden berücksichtigt. Dieses Modell ist auf den Fall sehr verdünnter Lösungen, wo keine Wechselwirkung zwischen zwei Ketten auftritt, beschränkt. Da es praktisch unmöglich wurde die verschiedenen Konfigurationen darzustellen (mehr als 3000), wurde eine Populationsstatistik von Ketten der Länge n, die aus Ketten der Länge $n/2$ zufallsmässig gebildet wurden, durchgeführt. Weiters wurde die Abhängigkeit des Kettenenden-Abstands von der Natur des Copolymeren und den Eigenschaften der Bausteine bestimmt. Es wurde versucht, auf ein Netz mit beliebiger Koordinationszahl zu verallgemeinern und eine Beziehung für die Abhängigkeit der Tahl der Konfigurationen einer Kette der Länge n von n aufzustellen.

Discussion

H. Benoit (*C.R.M., Strasbourg, France*): Croyez-vous qu'il soit possible de généraliser aux réseaux à trois dimensions les résultats que vous avez obtenus sur un réseau à deux

dimensions? Serait-il possible de tenir compte des interactions en donnant des poids statistiques différents de zéro et un?

M. Lautout-Magat: Il est possible de généraliser mes résultats en dénombrant les configurations sur un réseau à 3 dimensions. Le nombre de configurations devenant rapidement enorme, ce travail ne peut être fait que par de machines. Les cas particuliers pour lesquels j'ai dessiné les configurations pourront servir à verifier le programme. Pour de très courtes longueurs de chaîne, j'ai verifié que le sens de variation du nombre de configurations avec le type du copolymère est le même pour un réseau à 2 ou à 3 dimensions. On peut évidemment tenir compte des interactions en donnant un poids statistique different de 0 ou 1 aux differentes configurations. C'est la deuxième approximation dont je parlais tout à l'heure et que je termine actuellement.

J. J. Hermans (*Chemstrand, Durham, North Carolina*): Si j'ai bien compris votre calcul, on ne peut pas disposer un monomère à coté d'un voisin incompatible. D'autre part le réseau est un réseau bien défini dans lequel le nombre de voisins est fini. Que faiton dans le calcul quand un monomère ne trouve plus de "places compatibles?" Est-ce qu'il faut terminer la chaine à ce point?

M. Lautout-Magat: Parmi les types particuliers de copolymères que j'ai étudiés, le cas où la seule place possible sur le réseau pour le monomère est une "place incompatible" se présente surtout pour le copolymère alterné $(AB)_n$ A soluble, B mal soluble. Cette situation se produit environ 3 fois sur 1000 pour les chaînes de 20 segments. Etant donné la faible fréquence d'apparition de ces configurations, je termine la chaîne en ce point d'autant plus que, pour la continuer, il faudrait placer le monomère sur un site où il serait voisin premier, non seulement de un, mais le plus souvent de 2 ou 3 segments de nature différente

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Étude de Copolymères Greffés et Séquencés en Solution

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INTRODUCTION

L'intérêt suscité récemment par les copolymères greffés et séquencés provient en grande partie du fait que leurs propriétés sont originales, alors que celles des copolymères "statistiques," sont le plus souvent intermédiaires entre celles des homopolymères constitutifs.

Cependant l'étude du comportement physicochimique de copolymères greffés et séquencés en solution en est encore à ses débuts car le nombre important des paramètres à considérer rend difficile l'interprétation des résultats. A côté de la composition globale de l'échantillon, il faut aussi tenir compte ici du nombre et de la longueur des séquences, de leur mode d'enchaînement, de leur comportement individuel par rapport au solvant et des interactions, qui existent entre séquences de nature chimique différente.

Incompatibilité entre Chaînes Macromoléculaires de Nature différente

On sait qu'en général quand on essaye de dissoudre deux polymères différents dans un même solvant, un trouble apparaît. Cette démixtion[1] montre qu'il existe des répulsions entre chaînes polymériques de nature différente. Ces répulsions doivent aussi se manifester quand les deux types de monomères font partie d'une même chaîne. S'il s'agit d'un copolymère statistique elles s'exerceront également sur toute la longueur de la chaîne[2] et en première approximation on pourra traiter le copolymère comme un nouveau type de polymère. Si au contraire on a un polymère formé d'un petit nombre de séquences, de nature chimique différente il est probable que les effets seront tout-à-fait différents et qu'on aura pour cet échantillon un comportement entièrement nouveau.

Ces données qualitatives ont été récemment précisées par Burnett, Meares, et Paton.[3] Ces auteurs ont étudié le comportement viscosimétrique et osmotique de copolymères séquencés styrène–méthacrylate de méthyle, en solution dans le toluène, bon solvant des deux types de séquences. Ils ont cherché à caractériser la variation des paramètres thermodynamiques et configurationnels avec la composition du copolymère et ils ont constaté que ce n'est qu'en postulant l'existence de répulsions entre segments de chaîne de nature différente que l'on pouvait expliquer l'en-

semble des résultats expérimentaux. Ces auteurs vont même jusqu'à envisager une séparation de phase intramoléculaire, analogue à la démixtion que l'on observe dans le cas de solution de mélanges d'homopolymères dans un solvant commun.

Etude des Copolymères en Milieu Solvant Préférentiel

On peut aussi examiner le comportement de copolymères greffés et séquencés en solution non pas dans un bon solvant des deux types de séquences A et B, mais dans un liquide qui marque une affinité préférentielle—voire même exclusive—pour l'un des types de séquences, que par convention nous appellerons A.

Le problème n'en est pas rendu plus simple pour autant, mais son intérêt est plus évident, car l'action conjuguée des répulsions entre séquences différentes et de l'affinité préférentielle du solvant peut amener la formation de configurations nouvelles, et même, de phases nouvelles.

C'est de qui a été démontré par une étude systématique effectuée au CRM par Skoulios et son groupe.[4–7] En présence de solvants préférentiels ou sélectifs, les gels de copolymères séquencés présentent, selon les conditions expérimentales, plusieurs types de phases biréfringentes. Dans ces gels mésomorphes, les contacts entre éléments de chaîne différents sont réduits au minimum, c'est-à-dire pratiquement aux seules liaisons chimiques entre séquences différentes, celles-ci occupant des domaines de l'espace distincts:

Dans le cas des solutions diluées et moyennement concentrées, on peut à priori envisager plusieurs types de structures.

(*1*) Si les séquences A d'une molécule sont trop courtes ou trop peu nombreuses, ou que leur affinité pour le liquide S est trop faible, la mise en solution du polymère s'avère impossible.

(*2*) Si la solvatation des séquences solubles est suffisante pour entraîner la mise en solution de l'ensemble on doit pouvoir arriver à une dispersion moléculaire, mais la solution n'en conserve pas moins certaines caractéristiques des solutions micellaires: la partie (B) insoluble—ou mal soluble—de la molécule peut se comparer avec un petit morceau de gel maintenu en solution par les séquences A solubles, solvatées, qui forment autour de lui un volume de protection.

(*3*) On peut envisager un cas intermédiaire: les séquences solubles A de plusieurs molécules s'associent pour parvenir à la mise en solution des parties insolubles correspondantes: la dispersion est polymoléculaire, la solution est micellaire.

Nous verrons que l'expérience a permis d'étayer ces hypothèses et qu'en fait nous avons pu rencontrer les trois cas indiqués ci-dessus, selon la nature des copolymères, des solvants utilisés et les concentrations. Nous avons recherché également si, en solution de concentration intermédiaire, la formation de micelles anisotropes ne préfigure pas le gel mésomorphe auquel donneraient naissance les micelles en s'associant.

Les considérations qui précèdent nous semblent devoir justifier l'étude entreprise des solutions de copolymères greffés et séquencés en milieu solvant préférentiel. Dans le domaine des solutions diluées nous avons cherché à déterminer l'influence des interactions solvant–soluté et des répulsions entre séquences incompatibles sur les configurations de la molécule et son architecture interne. C'est ensuite la formation d'agrégats, étape intermédiaire entre la solution isotrope et le gel mésomorphe qui a retenu notre attention.

PARTIE EXPERIMENTALE

Préparation des Copolymères

Ce n'est que depuis peu d'années que l'on se préoccupe des méthodes spécifiques de préparation de copolymères séquencés et greffés. Smets et Hart[8] évoquent dans une revue récente diverses méthodes d'obtention basées les unes sur des processus radicalaires de polymérisation, les autres sur des réactions chimiques entre macromolécules. Récemment Burnett, Meares, et Paton[9] ont réalisé la polymérisation sucessive de deux monomères différents par un même catalyseur bifonctionnel et ont ainsi obtenu des copolymères séquencés.

A ces méthodes radicalaires ou chimiques nous avons préféré des précédés d'obtention basés sur la polymérisation anonique en phase homogène de Szwarc.[10] L'absence de réaction de terminaison spontanée, qui caractérise cette méthode, peut être utilisée pour la préparation de copolymères séquencés et greffés.

(*1*) Pour obtenir des copolymères "en blocs" il suffit d'utiliser le polymère ω-carbanionique A^- comme initiateur pour la polymérisation du monomère b. On obtient ainsi des copolymères à 2 séquences AB, ou à 3 blocs BAB, selon la fonctionnalité de l'initiateur. Cette méthode a été décrite par Rembaum et Szwarc[11] et a été appliquée avec succès à de nombreux couples de monomères.[12] La préparation et la purification des copolymères séquencés styrène–oxyde d'éthylène ont déjà été décrites par ailleurs.[13]

(*2*) Pour la préparation de copolymères greffés par voie anionique deux méthodes peuvent être utilisées: le greffage par initiation carbanionique[14–16] et le greffage par desactivation carbanionique.[17,18] C'est ce deuxième procédé que nous avons utilisé dans le présent travail car il présente, sur le premier, l'avantage de donner naissance à des produits relativement bien définis. Il consiste à faire réagir en solution un polymère "vivant" ω-carbanionique monofonctionnel (I) sur un polymère II dont la chaîne porte des fonctions susceptibles de réagir sur les extrémités organométalliques du polymère "vivant." Il y a ainsi fixation de greffons I sur la chaîne macromoléculaire du polymère II. Des copolymères styrène sur méthacrylate de méthyle ont ainsi pu être obtenus dans de bonnes conditions. Le taux de greffage (proportion des fonctions ester ayant réagi) ne dépasse pas 10% et il est d'autant moins élevé que la masse

moléculaire du polymère–support est plus grande. Si la polydispersité du polymère–support est faible, le copolymère peut être considéré comme homogène en composition.

Lorsqu'on effectue le fractionnement des produits bruts, qui contiennent souvent quelque 20% de polystyrène de faible masse, non greffé, il faut veiller à ce que l'action, sur la solubilité, des facteurs masse moléculaire et composition se conjugue: l'homopolystyrène doit précipiter en dernier. Nous avons utilisé une méthode de fractionnement due à Mita[19] qui utilise un mélange chlorobenzène–benzène (1/1) comme solvant et l'éther de pétrole comme précipitant. L'extraction sélective, préconisée par les auteurs russes,[18] ne peut se justifier dans le cas des copolymères greffés.

Etude Physico-Chimique

Principe. Soit un copolymère binaire AB dont la molécule est formée d'un petit nombre de séquences homopolymères (ou de greffons) attachées les unes aux autres. Supposons-le en solution dans un liquide S qui est un bon solvant des séquences A comme des séquences B. Agissons à présent en sorte que la solubilité des séquences dans le liquide se différencie: les blocs A y restent solubles cependent que les séquences B voient leur affinité pour le liquide S décroître peu à peu. On observe les propriétés de la solution au fur et à mesure que se déroule la "précipitation interne" des séquences B, et on détermine si la solution reste moléculairement dispersée où si au contraire des agrégats se forment.

Pour agir sélectivement sur la solubilité d'un des types de séquences on peut procéder de deux manières différentes.

(*1*) On peut utiliser un mélange de deux liquides S_1 et S_2, S_1 étant un solvant de toutes les séquences et S_2 un précipitant sélectif des séquences B. S_1 et S_2 sont choisis de telle sorte que leurs dimensions moléculaires et leurs indices de réfraction soient aussi voisins que possibles. Les courbes donnant la viscosité intrinsèque du copolymère en fonction de la composition du mélange de solvants rendent compte de la contraction de la molécule de copolymère. Nous avons utilisé des mélanges de dioxanne S_1 et de cyclohexane S_2 comme milieu solvant, en prenant soin d'opérer à 35°C, température θ du polystyrène dans le cyclohexane.

(*2*) On peut aussi choisir un liquide unique S qui soit à la fois bon solvant des séquences A et solvant θ—à la température θ—des séquences B. On effectue les mesures de viscosité et de diffusion de la lumière à différentes températures, situées de part et d'autre de la température θ. La courbe $[\eta]$–T illustre la contraction de la molécule.

Les deux méthodes donnent, nous le verrons, des résultats comparables. Mais il convient de préciser les avantages et inconvénients de chacun des procédés permettant de faire varier la solubilité des séquences B du copolymère.

(*1*) La méthode qui utilise des mélanges de deux liquides est d'un usage immédiat: on travaille à température constante. L'inconvénient de cette méthode réside dans l'adsorption sélective, par les différentes séquences,

du meilleur solvant. Ce phénomène est parfois important et il peut fausser certaines conclusions. Mais les résultats de diffusion de la lumière ne sont pas affectés par l'adsorption préférentielle car solvant et précipitant ont même indice de réfraction: aussi la formation d'aggrégats ne peut-elle pas passer inaperçue.

(*2*) La méthode du solvant θ est en théorie la meilleure, mais elle est délicate à utiliser, car il faut tenir compte de la variation, en fonction de T, de la viscosité intrinsèque des homopolymères pour pouvoir interpréter les diagrammes $[\eta]$–T obtenus. Il est d'ailleurs difficile de trouver un liquide qui soit simultanément solvant-θ d'une séquence, et bon solvant de l'autre, dans toute l'étendue du domaine de température envisagé.

Appareillage. Les mesures de diffusion de la lumiere ont été effectuées à l'aide d'un photogoniodiffusomètre Sofica thermostaté. La température doit en effet être maintenue avec précision car la concentration à partir de laquelle on peut mettre en évidence des agrégats polymoléculaires en solution, varie notablement avec la température. L'incrément d'indice est déterminé à l'aide d'un réfractomètre différentiel Brice-Phoenix.

Les mesures de la viscosité intrinsèque ont été effectuées au capillaire dans un appareillage décrit par Vallet[20] et thermostaté au 1/20^e de degré.

Des mesures de biréfringence électrique (effet Kerr) ont été effectuées sur certaines de nos solutions micellaires au moyen de l'appareil mis au point et décrit par Benoit.[21]

Solvants. Tous les solvants ont ete soigneusement séchés, filtrés, distillés et dépoussiérés avant utilisation. Leurs indices de réfraction ont été contrôlés et leur teneur résiduelle en eau déterminée par la méthode de K. Fischer.

TABLEAU I

Réf.	Type	Styene, %	B, %	B	M_w copolymère	M_w styrène ds. copolymère
600	Séq. BAB	59	41	Méthacrylate de méthyle	440.000	260.000
825	Séq. AB	40	60	Oxyde d'éthylène	16.700	6.700
838	Séq. AB	60	40	Oxyde d'éthylène	14.000	8.300
831	Séq. AB	71	29	Oxyde d'éthylène	35.000	25.000
Y_{A1}[a]	Greffé $M_{greffon}$ = 30.500, M_{PMMA} = 98.000)	88,6	11,4	Méthacrylate de méthyle	638.000	540.000
Y_G[a]	Greffé $M_{greffon}$ = 30.000, M_{PMMA} = 600.000)	56,1	43,9	Méthacrylate de méthyle	1.1×10^6	500.000

[a] Solvent THF; Initiateur phénylisopropyl K.

TABLEAU II

Points de Précipitation des Copolymères dans les Mélanges Dioxanne–Cyclohexane

Polymère	MMA, %	Cyclohexane, %	M
Homo-PMMA		45–55	
Copolymère statistique	46	70	245.000
Copolymère séquencé	BAB, 41	60	440.000
Copolymères greffés			
Y_G	44	92	1.100.000
Y_{A1}	89	98	640.000

TABLEAU III

Mesures de Diffusion de la Lumière sur les Copolymères Greffés Y_{A1} et Y_G en Milieu Dioxanne–Cyclohexane (Fig. 1)

Solvant		Copolymère Y_G			Copolymère Y_{A1}	
Dioxanne, %	Cyclohexane, %	$\bar{M}_w$	$(\overline{\rho^2})^{1/2}$, A	k	$\bar{M}_w$	$(\overline{\rho^2})^{1/2}$, A
100	—	$1{,}1 \times 10^6$	446	1	660.000	280
40	60	$1{,}3 \times 10^6$	202	1,2		
30	70	$2{,}9 \times 10^6$	242	2,6		
20	80	$3{,}0 \times 10^6$	167	2,7		
10	90	$5{,}2 \times 10^6$	230	4,7	650.000	186
5	95				650.000	160

TABLEAU IV

Viscosités Intrinsèques de Copolymères Séquencés et Greffés poly styrène–PMMA dans les Mélanges Dioxanne–Cyclohexane à 35°C (Fig. 2)

Cyclohexane, %	[η] Copolymères polystyrène–PMMA			[η] Homopolymères		
				Polystyrène	PMMA	
	Séq. 600	Y_{A1} greffé	Y_G greffé	M = 30.500	M = 600.000	M = 98.000
0	77	59	130	19,5	128,5	35
10	77	59	130			
20	77	59	130	19,5	123	33
30	75	59	118			
40	70	59	95,5		86	26,5
46					63	
50	62	57,5	74,5			21,5
53						18,5
60	50	50	32,6			
70		43	25	19,5		
80		35	23	17,5		
90		25	16			
95		22,5				
98		20				
100				15,0		

RÉSULTATS EXPÉRIMENTAUX

Au Tableau I nous avons fait figurer la liste des polymères sur lesquels a porté la présente étude.

Les points de précipitation des divers copolymères styrène–méthacrylate de méthyle dans les mélanges dioxanne–cyclohexane sont donnés au Tableau II. Les résultats des mesures de diffusion de la lumière dans ces mêmes mélanges sont consignés au Tableau III. Les Tableaux IV–VI donnent les résultats des mesures de viscosité. Enfin le Tableau VII contient les données relatives aux mesures de diffusion de la lumière effectuées sur les copolymères styrène–oxyde d'éthylène en solution dans l'éthylbenzène.

TABLEAU V
Viscosité Intrinsèque du Copolymère 825 Styrène–Oxyde d'Ethylène

Solvant			Oxalate d'éthyle	
Cyclohexane	Dioxanne	$[\eta]$	T,°C	$[\eta]^a$
	100	22,2	70	18,5
50	50	20,1	51,5[b]	18,3
65	35[c]	16,5	30	18,2

[a] Dans l'oxalate d'éthyle.
[b] Température θ du polystyrène en solution dans l'oxalate d'éthyle.
[c] Au-delà il y a précipitation.

TABLEAU VI
Viscosité Intrinsèque de Copolymères Greffés en Solution dans l'Acétate d'isoamyle (Fig. 3)

	Copolymère Y$_G$		Polyméthacrylate de méthyle	Polystyrène
T,°C	$[\eta]$	M_w[a]	$[\eta]$	$[\eta]$
100	42.5		55	
90	42			
80	39.5	$1{,}0 \times 10^6$		15,5
70	33		46	
60	29.5	$1{,}1 \times 10^6$		
50	29		39,5	
40	28			
30	27	$1{,}1 \times 10^6$	31	
20	25	$1{,}1 \times 10^6$		15

[a] Ces valeurs ont été obtenues par diffusion de la lumière, dans l'acétate disoamyle pour différentes températures.

DISCUSSION DES RÉSULTATS EXPÉRIMENTAUX

Nous examinerons successivement les résultats de nos mesures effectuées en solution dans des mélanges binaires et ceux relatifs aux expériences conduites en milieu solvant préférentiel.

TABLEAU VII

Résultats de Diffusion de la Lumière: Copolymère 831 Styrène–Oxyde d'Éthylène, Solvant Éthylbenzène[a]

Temperature, °C	Concentration, g/cm³ · 10²	Valeur de c/I extrapolée à angle nul $(c/I)_{\Theta=0} \times 10^4$	Dissymétrie I_{45}/I_{135}	Dépolarisaton $(\rho_u)_{90°}$
60	0,217	0,90	1,00	0
	0,434	0,80	1,17	0
	0,975	0,60	1,40	0,05
	1,300	0,55	1,60	0,05
	1,950	0,25	2,00	0,14
45	0,220	0,96	1,00	0
	0,440	1,02	1,19	0
	0,990	0,70	1,38	0,03
	1,320	0,50	1,60	0,06
	1,980	0,25	2,00	0,16
35	0,222	1,06	1,00	0
	0,444	1,17	1,10	0
	0,998	0,40	1,86	0,03
	1,332	0,30	2,20	0,05
	1,996	0,30	2,50	0,11

[a] Nous ne pouvons affirmer pour ces résultats qu'ils aient été obtenus sur des solutions en état d'équilibre thermodynamique. Signalons à titre d'exemple qu'à 25°C les solutions sont opalescentes au point de rendre impossible toute mesure de diffusion de la lumière. Cependant cette opalescence met quelque 3 jours à s'établir lorsque les solutions ont été préalablement chauffées à plus de 30°C. Les solutions ont été placées pendant 24 *h* dans une étuve thermostatée à la température prévue pour la mesure, et nous avons admis alors que les valeurs de l'intensité obtenues ne variaient plus de façon appréciable avec le temps.

Mesures Effectueés sur les Copolymères en Solution dans des Mélanges Dioxanne–Cyclohexane

Adsorption Préferentielle. Nous constatons que le dioxanne est adsorbé sélectivement sur les chaînes de polystyrène: la viscosité intrinsèque de l'homopolystyrène reste inchangée jusqu'à des teneurs en cyclohexane de l'ordre de 70%. L'adsorption sélective du dioxanne sur le polyméthacrylate de méthyle semble être un phénomène de bien moindre importance.

Etude du Point de Précipitation. Nous avons examiné les points de précipitation des différents copolymères et du polyméthacrylate de méthyle —c'est-à-dire les concentrations en précipitant pour lesquelles leurs solutions se troublent et floculent, (Tableau II). On constate que la "solubilisation" est de loin la meilleure dans le cas des copolymères greffés. Même dans le cas du produit Y_G de masse élevée ($1,1 \times 10^6$) et de taux de greffage faible (17 greffons polystyrène pour 6000 fonctions ester, soit 0,28%), la floculation n'intervient que pour des teneurs en cyclohexane supérieures à 90%.

Etude des Solutions au Voisinage du Point de Précipitation. Il ressort du Tableau III que les solutions du copolymère Y_{A1} sont moléculairement

dispersées jusqu'aux environs immédiats du point de précipitation (~98%), comme c'est le cas pour les solutions des homopolymères correspondants.

Dans le cas du copolymère Y_G il n'en est plus de même. Les résultats de diffusion de la lumière montrent qu'il y a association de plusieurs molécules de soluté en un agrégat dès que la teneur en précipitant atteint 60%. Bien que la solution reste limpide, la masse "moléculaire" du soluté augmente régulièrement jusqu'au point de précipitation (~92% en cyclohexane). Ces agrégats sont stables; il ne s'agit donc pas d'un début de précipitation.

Pour expliquer la différence de comportement de ces deux copolymères nous remarquerons que leurs taux de greffage sont différents, étant respectivement de 1,84% et 0,28%, bien que les greffons aient dans les deux cas

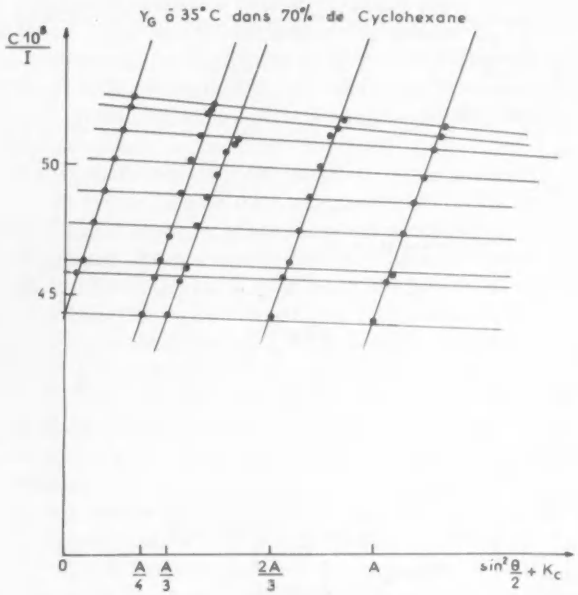

Figure 1.

pratiquement la même longueur moyenne. On peut donc supposer que dans le cas du copolymère Y_{A1} les 18 greffons de polystyrène assurent une protection suffisante de la chaîne de polyméthacrylate de méthyle: la solution reste donc moléculairement dispersée et on assiste à la formation de "micelles moléculaires."[22] Dans le cas du copolymère Y_G au contraire, la protection de la chaîne par ses greffons s'avère insuffisante: plusieurs chaînes de PMMA s'associent, forment un petit morceau de gel qui est maintenu en solution par l'action conjuguée de la totalité de leurs greffons. Il y a donc lieu de parler de "micelles plurimoléculaires" et le nombre

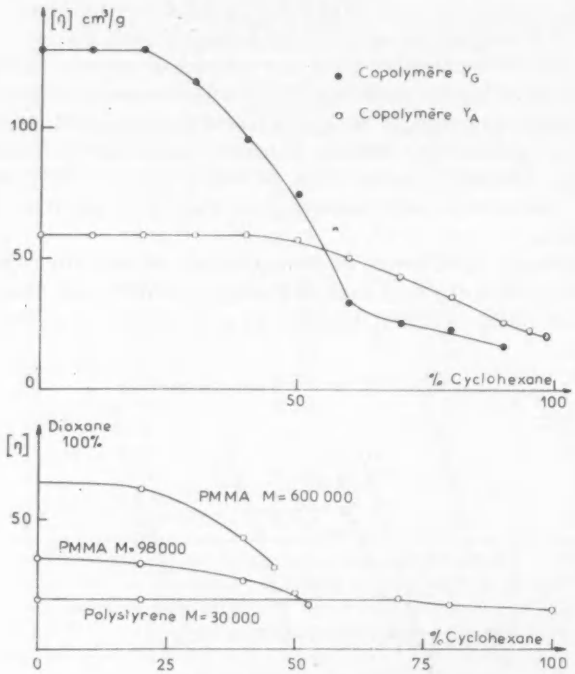

Figure 2.

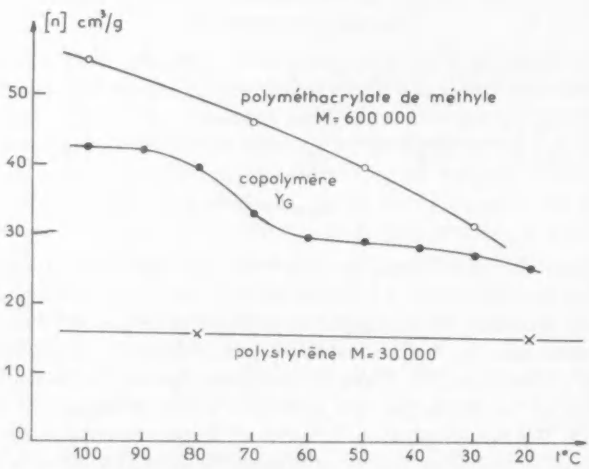

Figure 3.

moyen de molécules associées en un agrégat varie avec la teneur en cyclohexane du mélange de solvants.

Etude Viscosimétrique des Copolymères Greffés en Milieu Solvant Binaire. Si nous examinons les courbes donnant la viscosité intrinsèque des copolymères en fonction de la teneur en cyclohexane du mélange solvant, nous constatons en premier lieu que $[\eta]$ est constant jusqu'à une teneur de 45% en cyclohexane pour Y_{A1}, et de 20% pour Y_G. L'adsorption sélective du dioxanne par les greffons de polystyrène permet d'expliquer ce fait, mais il ne faut pas exclure la possibilité d'un effet de compensation entre les répulsions styrène—méthacrylate de méthyle et la contraction de la chaîne de PMMA sous l'effet du précipitant.

Quand la teneur en cyclohexane du mélange dépasse 45% (resp. 20%) la viscosité intrinsèque des copolymères décroît régulièrement. Elle atteint le tiers de sa valeur initiale dans le cas de Y_{A1} pour une teneur en précipitant sélectif de 98%. La viscosité intrinsèque du polymère Y_G à 60% de cyclohexane est environ environ le quart de ce qu'elle était dans le dioxanne pur; mais au-delà de cette teneur de 60% en précipitant la viscosité intrinsèque ne décroît plus que faiblement au fur et à mesure que progresse l'association des molécules de soluté.

Ces résultats appellent trois remarques.

(*1*) Climie et White[23] ont étudié récemment le comportement viscosimétrique de copolymères séquencés polyméthacrylate de méthyle–polyacrylonitrile en milieu solvant–précipitant pour les séquences de polyacrylonitrile. Ces auteurs estiment que la chute brutale de la viscosité qu'ils observent pour une composition déterminée du mélange DMF–benzène est due à la formation reversible d'agrégats polymoléculaires. Ici au contraire la formation d'agrégats ne semble pas entraîner de chute brutale de $[\eta]$. Mais il faut préciser que la protection d'une chaîne séquencée par les séquences solubles est inférieure à celle d'une chaîne greffée par les greffons solubles. Il pourrait donc s'agir d'un début de floculation dans le cas de Climite et White.

(*2*) Le fait que $[\eta]$ ne varie pas de façon notable quand il y a formation d'agrégats polymoléculaires nous paraît explicable. Nous avons vu,[22] en effet, qu'une "micelle moléculaire" peut être assimilée en pemière approximation à une étoile à n branches,[24] n étant le nombre de greffons. Ce faisant on néglige le volume propre de la chaîne de PMMA insoluble. Si p molécules s'associent pour former une micelle polymoléculaire, les p chaînes de PMMA forment un nodule insoluble autour duquel sont disposés les pn greffons de polystyrène solvatés. Si on assimile le nodule insoluble à un point, le rayon de giration de la particule—donc $[\eta]$—ne doit pas être affecté par l'association de plusieurs molécules. Il dépend seulement de la longueur du greffon. Ces résultats qualitatifs sont d'ailleurs confirmés par les valeurs du rayon de giration mesurées par diffusion de la lumière, qui figurent au Tableau III.

(*3*) Si, au lieu d'assimiler le squelette polyméthacrylate de méthyle à un point on admet qu'il se rassemble sous forme d'une sphérule de volume pro-

portionnel à la masse de PMMA qu'elle contient, on constate que le nombre de chaînes de polystyrène par unité de surface de la sphère augmente avec le degré d'association. Ceci explique pourquoi l'échantillon Y_G forme des agrégats polymoléculaires stables alors que l'échantillon Y_A reste dispersé moléculairement jusqu'au point de précipitation.

Cas des Copolymères Sequencés en Milieu Solvant Binaire. Le cyclohexane est également un précipitant des séquences polyoxyéthylène, aussi avons-nous utilisé le même mélange solvant–précipitant pour l'étude viscosimétrique du copolymère 825 styrène–oxyde d'éthylène. La diminution de $[\eta]$ que l'on observe quand on passe du dioxanne pur au mélange correspondant au seuil de précipitation est faible par rapport aus effets observés dans le cas des copolymères greffés. Les répulsions entre séquences de nature différente se manifestent ici comme là, mais l'effet de protection de la partie la moins soluble par la partie solvatée est forcément réduit car il n'y a qu'une séquence soluble par séquence insoluble, le copolymère étant de type AB.

Signalons à ce propos que Bresler[25] et ses collaborateurs ont étudié un copolymère styrène–isoprène à 9 séquences en présence de précipitants sélectifs de chacun des deux types de séquences. Selon eux, les séquences solubles d'une même molécule se groupent en se contractant, et forment un glomérule autour duquel sont réparties les séquences solubles qui maintiennent la molécule en solution. Il apparaît donc qu'un polymère polyséquencé a un comportement analogue à celui d'un polymère greffé et très différent de celui d'un copolymère à petit nombre de séquences.

Mesures Effectuées sur des Copolymères dans un Solvant Sélectif

Copolymères Greffés Styrène sur Méthacrylate de Méthyle. Les mesures de viscosité effectuées sur les solutions du copolymère Y_G dans l'acétate d'isoamyle corroborent dans l'ensemble les résultats de l'étude en mélange solvant précipitant. L'acétate d'isoamyle est un solvant θ du polyméthacrylate de méthyle à 70°C environ, mais les mesures demeurent possibles largement en-dessous de cette valeur, même sur l'homopolyméthacrylate de méthyle. L'effet de l'abaissement de la température sur la viscosité intrinsèque est plus important, aux environs de 70°C, dans le cas du copolymère que dans celui de l'homopolymère. Nous pensons que cela doit être attribué à l'action conjuguée des répulsions entre séquences de nature chimique différente et des interactions différenciées entre le solvant et les deux types de séquences.

Nous remarquerons que les valeurs de la viscosité intrinsèque du polyméthacrylate de méthyle sont supérieures, dans tout l'intervalle de température considéré, à celles du copolymère greffé construit sur la même chaîne de PMMA, et de masse presque double. A 100°C les produits $[\eta]\,M$—proportionnels aux volumes moléculaires—du copolymère Y_G et de l'homopolymère correspondant sont dans un rapport de 1,54; pour les dimensions linéaires de la molécule le rapport correspondant est de 1,15 . La faible valeur de ce rapport traduit bien le caractère ramifié de la molécule de co-

polymère greffé, mais peut-être indique-t-il également que la nature chimique différente des greffons conduit la chaîne principale de PMMA à se contracter; seule une étude systématique de la viscosité de copolymères en fonction du taux de greffage permettrait de trancher ce point.

Nous noterons enfin que la masse moléculaire du soluté ne varie pas avec la température. L'action différenciée du solvant sur les deux types de séquences n'est donc pas suffisante ici pour conduire à la formation d'agrégats polymoléculaires tels que ceux que nous avons observés sur le même copolymère en milieu solvant binaire quand la teneur en précipitant sélectif était élevée.

Copolymères Séquencés Styrène–Oxyde d'Éthylène. Lorsqu'on analyse les résultats de diffusion de la lumière obtenus sur ces copolymères et rassemblés dans le Tableau VII, on constate des anomalies très nettes dans le comportement des solutions.

Il semble qu'au-dessus d'une certaine concentration, qui dépend d'ailleurs de la température, il existe dans la solution des particules de masses et de dimensions élevées, sans doute très anisodiamétriques vu les valeurs élevées des facteurs de dépolarisation. Malheureusement il est difficile, au vu de ces résultats, de donner une description précise de la forme et des dimensions des particules en solution.

Il a été montré récemment que les solutions concentrées de copolymères amphiphiles (> 35%) dans des solvants sélectifs (tel l'éthylbenzène) de l'une des séquences se présentent sous la forme de gels biréfringents. On obtient ainsi des phases liquides–cristallines analogues à celles que présentent les solutions concentrées de savons. On sait d'autre part que les solutions diluées de savons sont moléculairement dispersées. Mais à une certaine concentration appelée concentration micellaire critique (CMC) on passe de la dispersion moléculaire à la solution micellaire. Il était tentant de chercher si l'analogie mise en évidence sur les gels se retrouvait en solution diluée et moyennement concentrée. Il nous semble que les résultats de diffusion de la lumière dont nous faisons état apportent quelques arguments en faveur de cette hypothèse. Mais les résultats sont trop fragmentaires pour que nous puissions affirmer l'existence d'une véritable concentration micellaire critique. Il se pourrait également que le nombre de molécules participant à une micelle dépende de la concentration, ce qui conduirait à un domaine critique plutôt qu'à une concentration critique. D'autre part dans le domaine des faibles concentrations où l'on n'observe ni dépolarisation ni disymétrie dans la répartition angulaire de la lumière diffusée, la solution doit être moléculairement dispersée. Les hétérogénéités en composition jointes à la faible valeur du dn/dc de notre polymère dans l'éthylbenzène peuvent être tenues pour responsables des valeurs trop élevées de $\bar{M}_w$ que l'on obtient à partir des résultats de diffusion de la lumière.[26]

Il fallait donc montrer qu'au dessus du domaine de concentration où apparaissent des anomalies mises en évidence par diffusion de la lumière il existait effectivement des agrégats dans la solution. Dans ce but nous

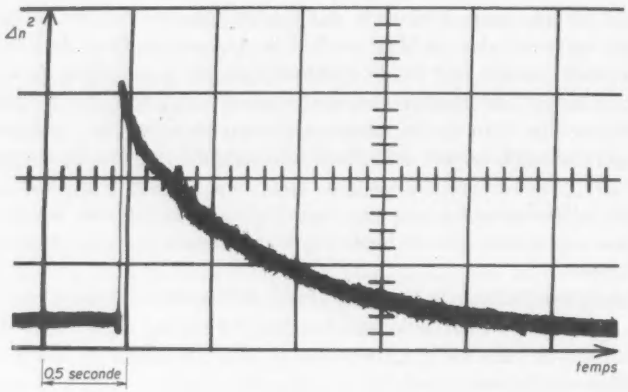

Figure 4.

avons fait une expérience qualitative de biréfringence d'écoulement qui nous a permis de mettre en évidence une biréfringence très élevée.

Pour préciser ce point, nous avons étudié par effet Kerr des solutions du copolymère 838 dans l'éthylbenzène à des concentrations de l'ordre 1%. On observe un effet Kerr important, mais qui présente la particularité d'avoir un temps de relaxation de plusieurs secondes. Ce temps de relaxation est difficilement explicable car il exige, si l'on admet qu'il s'agit d'une relaxation d'orientation, que les particules aient des dimensions très élevées (Fig. 4).

Afin de voir si le phénomène observé est général, nous avons repris les mêmes expériences en utilisant cette fois comme solvant le méthanol, qui est un bon solvant du POEG et un précipitant du polystyrène. On observe aussi un effet Kerr mesurable, moins intense que dans le cas précédent, et dont le temps de relaxation est considérablement plus faible puisqu'il est de l'ordre de 10^{-3} sec.

Bien qu'il ne s'agisse que d'expériences préliminaires on peut attribuer ces différences de comportement au fait que, dans l'éthylbenzène, les chaînes de POEG peuvent cristalliser[6] tandis que ce n'est le cas ni pour le polystyrène ni pour le POEG dans le méthanol.

CONCLUSION

Dans ce travail, nous venons de présenter un certain nombre d'expériences ayant pour but de caractériser les solutions de copolymères lorsque le milieu est un mauvais solvant pour l'un des types de séquences. Il aurait fallu, pour que ce travail soit complet, étudier systématiquement l'effet de la structure et de la composition de nos copolymères sur les propriétés de leurs solutions. Malgré le petit nombre d'exemples que nous avons pu étudier il semble que l'on puisse caractériser différents types de comportements bien distincts.

Si la partie insoluble ou mal soluble est protégée par de nombreuses chaînes latérales, ou par de nombreuses séquences bien solubles, les molécules forment ce que nous avons appelé des micelles moléculaires, dans lesquelles la molécule ressemble à une particule de gel maintenue en solu- par la partie solvatée.

Lorsque le milieu solvant différencie plus nettement encore les séquences, ou si la proportion de séquences solubles se révèle insuffisante, un nombre restreint de molécules est appelé à s'associer et l'agrégat polymoléculaire ainsi formé est maintenu en solution par l'action conjuguée des parties solubles de toutes les molécules. Ce type d'association évolue de façon continue avec la concentration de la solution, et les valeurs de la viscosité intrinsèque et du rayon de giration que nous avons obtenues permettent de préciser la structure de ces micelles plurimoléculaires.

Bien différent est le cas des copolymères séquencés de type BA ou ABA, dans lesquels l'effet de protection des séquences solubles sur celles qui ne le sont pas est beaucoup plus restreint. Ils floculent rapidement quand on ajoute un précipitant sélectif. Toutefois il a été possible de préparer des solutions de copolymères dans des solvants dont le caractère préférentiel est assez accusé et là encore l'association de plusieurs molécules en un agrégat semble être à l'origine de la stabilité de la dispersion. Mais la concentration et la température paraissent jouer ici un rôle important et c'est ce qui nous a conduit à faire un rapprochement avec les solutions micellaires de savon. Il se forme de gros agrégats, stables et anisodiamétriques, tout au moins au-dessus d'une certaine concentration, et ce phénomène est particulièrement net quand la séquence non (ou peu) soluble présente une tendance à la cristallisation.

Ces quelques expériences ont donc permis de mettre en évidence un certain nombre de structures que l'on ne rencontre jamais dans le cas des solutions des homopolymères. Il nous semble indispensable de poursuivre ces recherches afin de préciser les conditions d'existence de ces différentes structures et de voir si leur caractérisation ne permettrait pas de déterminer, dans un milieu solvant donné, les énergies d'interaction entre séquences de nature chimique différente.

Nous tenons à remercier très vivement M. le Professeur Charles Sadron pour l'intérêt soutenu qu'il a manifesté à ce travail et pour les conseils et suggestions qu'il nous a apportés. Nous remercions également M. A. Skoulios et M. le Professeur Mysels pour la part qu'ils ont prise à la discussion de nos résultats.

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Résumé

Dès études de viscosité et de diffusion de la lumière ont été effectuées sur des copolymères AB greffés et séquencés dans un solvant préférentiel des seules parties A. On a observé différents phénomènes, dépendant de la concentration de la solution, de la température et des solvants sélectifs employés. Aux faibles concentrations, la dispersion est toujours moléculaire mais les résultats de viscosité montrent que chaque molécule se comporte comme une micelle car la partie B insoluble, rassemblée sur elle-même, n'est maintenue en solution que par la partie soluble A qui empêche la précipitation. Si la concentration croît, ou si le rapport A/B est trop faible, une dispersion polymoléculaire apparaît. Le nombre de molécules associées dans une particule dépend non seulement de la température mais également du pouvoir de solvatation de A dans le solvant ou le mélange de solvants considéré. Des expériences préliminaires ont montré que dans certains cas, plus précisément lorsque la partie B peut cristalliser quand elle n'est pas solvatée, les agrégats sont hautement anisotropes, faisant apparaître une forte biréfringence lorsqu'ils sont placés dans un champ électrique ou hydrodynamique Ces phénomènes, observés dans notre laboratoire pour la première fois, doivent être mis en relation d'une part avec les fortes répulsions qui existent entre séquences de nature chimique différente et d'autre part avec les interactions différenciées entre le solvant et chacun des types de séquence.

Synopsis

Viscosity and light-scattering measurements on block and graft copolymers AB in solution in a better solvent of, say, part A, have been carried out. Different phenomena could be observed, depending upon the concentration of the solution, the temperature, and the selectiveness of the solvent used. At low concentrations the dispersion is always molecular, but viscosity data show that each molecule seems to be like a micelle, because

the insoluble part B has shrunk together and is maintained in solution by the soluble parts A which protect it from precipitation. If the concentration increases, or if the ratio A/B is too low, polymolecular dispersion shows up. The number of molecules associated in one particle is temperature-dependent and depends also upon the solvating power of A in the solvent or solvent mixture considered. Preliminary experiments have shown that in some cases, precisely when part B is able to crystallize if unsolvated, the aggregates are highly anisotropic, showing strong birefringence in hydrodynamic or electric fields. These phenomena which have been observed here for the first time must be related to the strong repulsions between chemically unlike blocks and to differentiated interactions between the solvent and each of the blocks.

Zusammenfassung

Lichtstreuung- und Viskositätsmessungen sind an Block und Pfropfkopolymeren in besseren Lösungsmitteln eines Teiles des Makromoleküls durchgeführt worden. Verschiedene neue Erscheinungen konnten beobachtet werden; die Temperatur, die Konzentration und die differentiale Löslichkeit der einzelnen Blöcke sind die für diese Arbeit herangezogenen Parameter. Wenn die Konzentration sehr klein ist, ist die Dispersion meistens molekular. Unter gewissen Umständen jedoch kann der unlöliche Teil sich abscheiden, aber doch als "molekulares Mizell" in Lösung bleiben, wenn die Löslichkeit der löslichen Blöcke dazu genügt. Wenn die Konzentration zu höheren Werten steigt, oder wenn das Verhältnis A/B ungünstig fällt, so tritt Assoziation hervor. Die Zahl der assoziierten Moleküle ist Temperaturabhängig und hängt auch von der Affinität der löslichen Blöcke für das Lösungsmittel ab. Wenn der unlösliche Teil des Makromoleküls kristallin werden kann, treten noch weitere neue Erscheinungen hervor: Die Partikeln, die aus assoziierten Molekülen bestehen, sind in diesem Falle hoch anisotrop. Die Lösungen zeigen Doppelbrechung wenn sie in einem Elektrischen Feld gestellt werden oder einem Stömungsgradient unterworfen werden. Die starken Abstossungen zwischen chemisch verschiedenen Blöcken und die differenzierten Wechselwirkungen zwichen dem Lösungsmittel und den einzelnen Blöcken sind die Parameter die wir in Betracht gezogen haben, um die beobachteten Phänomene mindestens qualitativ zu erläutern.

Discussion

N. A. Plate (*Université de Moscou, Moscou, U.R.S.S.*): Dans le Laboratoire de Chimie Macromoléculaire de l'Université de Moscou nous avons montré, il y a déjà quelques années, que quand on passe à la phase solide d'un copolymer greffé constitué de composants differents par leur propriétés physiqueset chimiques (par ex. le copolymère polystyrene–acide polyacrylique) il existe aussi une microseparation. Les calculs de changement de l'enthalpie et l'entropie ont montré qu'il existe une protection assez grande des chaînes principales par les greffons. Il nous semble que les resultats obtenus par Rempp dans les solutions diluées sont bien conformes à nos données concernant les solutions concentrées et le passage de la phase solide du copolymère greffé à une solution concentrée.

A. Rembaum (*California Institute of Technology, Pasadena, California*): The polymerization reaction for the formation of polystyrene polyethyleneoxide blocks requires a fairly high temperature and several days for completion. Did you observe any degradation of polystyrene during this time?

P. Rempp: The preparation of block polymers was performed according to a method derived from that of Richards and Szwarc. The addition of an excess of ethylene oxide to a solution of a monocarbanionic "living" polymer is carried out at −78°C., and thus alcoolate end-groups are formed. The reaction mixture is then transferred into a thick walled glass vessel and heated at 80°C. for 3 days. The homopolyoxyethylene which is formed together with the expected block copolymer has of course to be discarded, by water extraction or by any other suitable method (Fing, Rempp, and Parrod, *Bul. Soc. Chim.*, **1962,** 262).

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Fractionnement d'un Copolymère Greffé Polyisobutylène-Polystyrène Préparé par Voie Radiochimique

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I. INTRODUCTION

Le fractionnement d'un polymère permet d'obtenir des fractions dont les masses moléculaires ont une distribution plus homogène que celle de l'échantillon initial. L'étude de ces fractions peut dans certains cas donner des informations relatives à la structure du polymère initial et à la cinétique de sa formation.

Dans le cas des copolymères greffés, la polydispersité en masses moléculaires peut s'accompagner d'une polydispersité en compositions.[1,2] Il est donc intéressant de savoir comment s'effectue le fractionnement, c'est-à-dire quelle est la contribution de chacune de ces deux polydispersités. De plus, une polydispersité des structures peut aussi influencer les résultats; ceci est particulièrement vrai dans le cas de copolymères obtenus par greffage radiochimique car le mécanisme de cette réaction est complexe. L'objet du présent travail est le fractionnement d'un copolymère greffé polyisobutylène-polystyrène préparé par voie radiochimique et l'étude des fractions obtenues.

Notons que le terme "fractionnement" a souvent été utilisé pour désigner la séparation d'un copolymère greffé des homopolymères généralement présents dans le mélange réactionnel. Nous tenons à préciser que nous réservons le terme "fractionnement" à l'opération destinée à isoler des fractions plus homogènes en partant d'un copolymère greffé préalablement débarrassé des homopolymères.

Quelques études sur le fractionnement de copolymères greffés ont déjà paru.[3,4] Ces travaux concernent des copolymères greffés obtenus par voie chimique.

Dans cette communication préliminaire, nous décrivons brièvement la méthode de préparation des échantillons utilisés; nous donnons ensuite le principe de deux méthodes de fractionnement, puis quelques propriétés des fractions en solution.

II. PRÉPARATION DES ÉCHANTILLONS DE COPOLYMÈRE GREFFÉ

A. Synthèse Radiochimique

La synthèse des copolymères greffés par voie radiochimique peut être réalisée par quatre méthodes différentes.[5] Nous avons choisi la méthode "directe" qui consiste à irradier simultanément un polymère et un monomère vinylique. Le polymère utilisé était le polyisobutylène Vistanex LMMS (Esso Standard) pour lequel nous avons déterminé: $\bar{M}_n = 37.000$; $\bar{M}_w = 62.000$; le monomère était le styrène. Des solutions de polyisobutylène dans le styrène étaient soumises au rayonnement γ émis par la source de Cobalt-60 de 200 curies du Laboratoire de Chimie des Radiations du C.N.R.S. à Bellevue. Nous nous sommes placés dans les conditions optimales de greffage déterminées antérieurement.[6] La concentration initiale en polyisobutylène était de 40% en moles, le taux de conversion était arrêté à environ 25%, l'intensité du rayonnement était d'environ 3 rad/s. Les détails de la technique expérimentale ont déjà été décrits.[6]

B. Séparation du Copolymère Greffé des Homopolymères

Le produit de la réaction renfermait les trois polymères suivants: le polyisobutylène non transformé, le copolymère greffé et le polystyrène. Le copolymère greffé était isolé par une méthode d'extraction sélective.[6] L'hexane technique était utilisé pour extraire le polyisobutylène, le cyclohexane dissolvait sélectivement le copolymère greffé à 22°C; le résidu de cette deuxième extraction était du polystyrène pur.

C. Caractérisation des Copolymères Greffés

Le copolymère greffé ainsi que, ultérieurement, les fractions ont été caractérisés de la facon suivante.

(*a*) La composition moyenne $\bar{X}$, exprimée en pour cent de styrène (en poids), était déterminée à partir de son absorption optique à 2620 A.[6]

(*b*) L'indice de viscosité limite $[\eta]$ était déduit des mesures de viscosité à 25°C dans le benzène. Le viscosimètre utilisé était du type Ubbelhode.

(*c*) Les masses moléculaires moyennes en nombre $\bar{M}_n$ étaient déterminées par osmométrie à 25°C à l'aide d'un osmomètre du type Pinner et Stabin[7] (fabriqué par Polymer Consultants Ltd.) équipé de membranes Pecel 600.

(*d*) Les masses moléculaires moyennes en poids $\bar{M}_w$ étaient mesurées au moyen d'un photogoniodiffusiomètre (appareil de Wippler et Scheibling[8] fabriqué par SOFICA). Les masses moléculaires apparentes[2] étaient déterminées dans le benzène par la méthode d'extrapolation à angle et concentration nuls due à Zimm.

Les caractéristiques des échantillons non fractionnés sont les suivantes: composition $\bar{X}$ = 77–92% de styrène; indice de viscosité limite $[\eta]$ = 52,5–57,5 cm³/g; masse moléculaire moyenne en nombre dans le benzène

$\bar{M}_n$ = 78.300–104.00; masse moléculaire moyenne en poids dans le benzène $\bar{M}_w$ = 189.000–205.000.

III. FRACTIONNEMENT DU COPOLYMÈRE GREFFÉ

Deux méthodes de fractionnement ont été utilisées: une précipitation fractionnée et une élution fractionnée sur colonne à gradient thermique.

A. Précipitation Fractionnée

Le fractionnement a été effectué en partant d'une solution du copolymère dans le cyclohexane, le précipitant choisi étant le *n*-propanol. Le couple cyclohexane–propanol offre en effet un large domaine de miscibilité totale à la température de 25°C choisie pour le fractionnement. Le fractionnement était réalisé à l'air libre. Les solvants employés étaient monodistillés. L'appareil comprenait un récipient conique muni d'un agitateur mécanique et d'un entonnoir par lequel on ajoutait des quantités connues de précipitant à l'aide d'une burette. Le récipient conique était plongé dans un thermostat reglé à 25°C. La concentration de la solution initiale était de 0,5%. Le mode opératoire correspondait à la technique classique avec les modifications suivantes: (*a*) la plupart des fractions étaient recueillies par centrifugation; (*b*) la composition du mélange solvant-précipitant en équilibre avec chaque fraction était déterminée par une méthode réfractométrique.

Technique Opératoire. A une solution de l'échantillon dans le cyclohexane S_1, on ajoutait progressivement de petites quantités de *n*-propanol jusqu'à l'apparition d'un trouble. Le polymère ainsi précipité ne décantait généralement pas de lui-même, même après plusieurs jours de repos. La fraction était donc extraite par centrifugation à une température contrôlée qui était identique pour toutes les fractions. Le précipité ainsi séparé était redissous dans le cyclohexane pour former une solution S_{1a}. Celle-ci était reprécipitée par la quantité de propanol juste nécessaire pour reproduire le γ d'apparition du trouble dans la première solution (rappelons que l'on désigne par γ de précipitation le rapport du volume de précipitant au volume total). Après une nouvelle centrifugation dans les conditions standard, le précipité était séché et pesé. Le filtrat était ajouté à la solution S_1, formant ainsi la solution S_2. Les mêmes opérations étaient répétées avec les solutions S_2, S_3, etc.

L'obtention de chaque fraction demandait 3 à 4 jours aussi pour le 2 è fractionnement, le rapport γ était-il contrôlé au fur et à mesure du déroulement des diverses opérations afin de mettre en évidence des variations éventuelles de concentration dues aux pertes par évaporation et par transvasement. Ce contrôle de la composition s'effectuait par un dosage réfractométrique. On avait préalablement établi la courbe d'étalonnage composition-indice de réfraction et vérifié que de faibles quantités de copolymère n'influaient pas sur les valeurs des indices. On opérait avec la

raie D du sodium, à l'aide d'un réfractomètre du type Pulfrich, thermostaté à 25°C.

L'ensemble de ces opérations est schématisé ci-dessous:

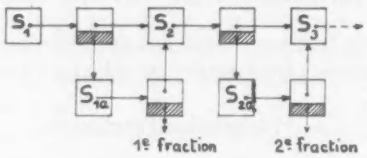


Figure 1.

Nous avons effectué deux fractionnements par cette méthode. Un premier échantillon (copolymère greffé H, pesant 1 g) était séparé en 9 fractions; un deuxième échantillon (copolymère greffé K, pesant 5 g) était séparé en 6 fractions dont certaines ont été sous-fractionnées. Les deux fractionnements étaient concordants dans leur ensemble. Les Tableaux I et II résument ces résultats.

TABLEAU I

Fractionnement par Précipitation

Copolymère H: $\bar{X}$ = 90.0% de Styrène, $\bar{M}_w$ = 189.000

Fraction No.	γ	Poids de la fraction, g	$\bar{X}$, % styrène	$[\eta]$ benzène	Observations
1	0,166	0,146	86,7	88,2	Suspension
2	0,177	0,138	87,8	74,2	Stable
3	0,225	0,218	85,5	61,0	"
4	0,255	0,149	83,2	49,1	"
5	0,268	0,020	86,9	—	"
6	0,287	0,129	82,3	40,6	"
7	0,381	0,073	77,1	—	Décantation
8	0,437	0,021	44,8	—	spontanée
9	0,570	0,075	—	—	"

Au cours de ces deux fractionnements, nous avons observé que les dernières fractions décantaient spontanément tandis que, comme nous l'avons signalé ci-dessus, il fallait recourir à la centrifugation pour séparer le polymère de toutes les autres fractions. Ce changement de comportement se produisait pour un γ de précipitation de l'ordre de 0,300–0,400. Nous avons retrouvé un phénomène analogue dans la deuxième méthode de fractionnement (voir ci-dessous).

B. Elution Fractionnée

Principe de la Méthode. Un grand nombre d'études ont déjà paru sur le fractionnement des homopolymères par élution sur colonne.[3,9–13] Dans cette méthode développée par Baker et Williams,[14] des précipitations et

TABLEAU II
Fractionnement par Précipitation
Copolymère K: $\bar{X}$ = 92% de Styrene

Fraction No.	γ	Poids de la fraction, g	$\bar{X}$ % styrène	$[\eta]$ benzène	$\bar{M}_n$	$\bar{M}_w$	Observations
FI	0,119	0,901	—	—	—	—	Suspension stable
FII	0,110	0,605	95,8	86,2	—	387.500	"
FI2	0,155	0,171	—	69,1	—	—	"
F2	0,160	0,416	87,8[a]	80,0	266.300	315.000	"
F3	0,195	0,964	95,0[a]	69,1	220.000	222.200	"
F4	0,250	0,895	97,7	58,8	144.600	156.300	"
F5	0,405	1,563	—	—	—	—	Décantation spontanée
F51	0,245	0,508	89,4	47,1	109.050	132.100	Suspension stable
F52	0,300	0,459	86,2	46,6	—	94.000	Décantation spontanée
F53	0,350	0,118	77,5	—	—	—	"
F54	0,395	0,051	—	22,6	—	—	"
F6	0,520	0,158	60,9	33,4	—	—	"

[a] Composition obtenue par microanalyse.

extractions fractionnées successives sont réalisées simultanément en une seule opération. Le polymère à fractionner est introduit au sommet d'une colonne remplie d'un matériau inerte vis-à-vis du polymère (poudre de verre). La colonne est alimentée par un éluant qui, au départ, est un précipitant du polymère et qui s'enrichit ensuite progressivement en bon solvant du polymère (gradient logarithmique de concentrations). La température de la colonne diminue de haut en bas (gradient linéaire de températures).

En chaque point de la colonne, il s'établit un équilibre entre le polymère précipité et le polymère dissous. Cet équilibre est déterminé par la composition du mélange éluant à chaque instant et par la température qui règne en ce point de la colonne. Au fur et à mesure du cheminement vers le bas de la colonne, le polymère tend à précipiter en raison de l'abaissement de la température et à se redissoudre car l'éluant s'enrichit progressivement en bon solvant. Ces conditions favorisent le bon fractionnement du polymère. Il est à noter que dans cette méthode, ce sont les fractions les plus solubles (les chaînes les plus courtes) qui sont éluées les premières.

Description de l'Appareil. Notre appareil comprend une colonne de verre de 50 cm de hauteur et de 36 m/m de diamètre intérieur. Cette colonne est remplie de poudre de verre tamisée, le diamètre des grains étant compris entre 100 et 160 μ.

Un manchon d'aluminium adapté autour de la colonne est chauffé à son sommet à 60 ± 0,1°C grâce à une résistance de 150 watts et refroidi à sa

base par une circulation d'eau thermostatée à 25 ± 0,1°C. Nous avons vérifié à l'aide d'un thermocouple que le gradient de températures était linéaire en fonction de la hauteur et qu'il n'y avait pas de gradient radial à l'intérieur de la colonne.

Le solvant est additionné en continu au précipitant dans un "flacon mélangeur" à volume constant, muni d'un agitateur magnétique. Un tel dispostif conduit à un gradient logarithmique des concentrations dans la colonne.[12,15] Le réglage du débit d'écoulement est réalisé à l'aide d'un flacon de Mariotte. Le solvant et le précipitant sont dégazés par ébullition avant leur arrivée au flacon mélangeur. La Figure 2 représente l'ensemble de l'appareillage.

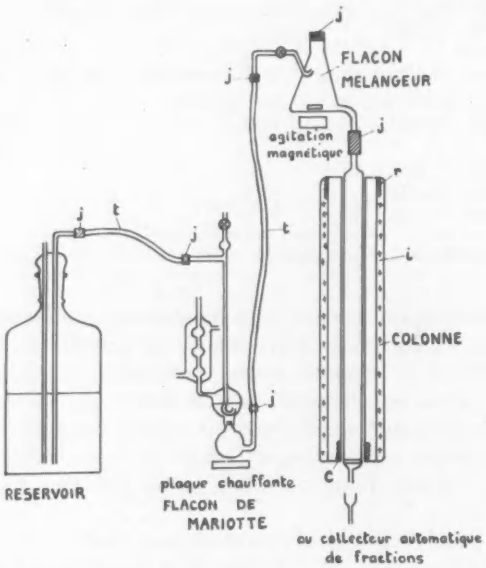


Fig. 2. Schéma d'ensemble de l'appareil de fractionnement par élution sur colonne: (c) circulation d'eau thermostatée; (i) isolant thermique; (j) joint Téflon verre; (r) résistance chauffante; (t) tube de Téflon souple.

Nous avons utilisé comme solvant le cyclohexane et comme précipitant l'isopropanol. La composition de l'éluant au cours du fractionnement peut être calculée à l'aide de l'équation suivante:[3]

$$(\gamma)_m = \gamma + \frac{V(\gamma^0 - \gamma^\infty)}{V_i - V_{i-1}} \left[\exp \frac{V_c - V_{i-1}}{V} - \exp \frac{V_c - V_i}{V} \right]$$

où $(\gamma)_m$ est le rapport moyen du volume de précipitant au volume total pour la fraction i, γ^∞ est le rapport du volume de précipitant au volume total dans le réservoir, γ^0 est le rapport du volume de précipitant au volume total

dans le flacon mélangeur au début de l'expérience, V est le volume du flacon mélangeur, V_e est la somme du volume interstitiel de la colonne et du volume mort de l'appareil compris entre le sommet de la colonne et la sortie du flacon mélangeur, et V_i est le volume total d'élution des i fractions.

Etude Expérimentale. Deux fractionnements ont été réalisés par cette méthode: sur un premier échantillon (copolymère greffé D pesant 2,23 g) et sur un deuxième échantillon (copolymère greffé D pesant 2,14 g). Des essais de solubilité avaient été effectués auparavant pour déterminer les conditions optimales de réussite.[13] Nous avons ainsi déterminé les valeurs suivantes des γ de précipitation critiques du copolymère greffé: complète solubilité à 25°C pour $\gamma = 0{,}087$; seuil de solubilité à 60°C pour $\gamma = 0{,}900$; complète précipitation à 25°C pour $\gamma = 0{,}500$.

Des fractions de 25 cm³ étaient séparées à l'aide d'un collecteur automatique de fractions à volume constant L.K.B. Chaque fraction était évaporée, le résidu était séché sous vide et pesé. Le Tableau III résume les données essentielles des deux fractionnements.

TABLEAU III
Conduite des Fractionnements sur Colonne

	Premier fractionnement copolymère D	Deuxième fractionnement copolymère D
Nombre de fractions	37	50
Vitesse moyenne d'écoulement, cm³/h	13	11,5
Volume du flacon mélangeur, cm³	300	525
Poids de polymère recueilli, g	2,227	2,037
Concentration maximum, g/100 cm³	1,37	0,97
Poids de la fraction minimale, g	0,0011	0,0011
Poids de la fraction maximale, g	0,3426	0,2419
Nombre de fractions de poids supérieur à 0,075 g	9	10
Polymère représenté par les fractions importantes, %	84,8	77,2

Nous avons constaté au cours des deux fractionnements qu'une partie du polymère contenu dans les fractions initiales [jusqu'à la 22ème fraction ($\gamma = 0{,}325$) pour le premier fractionnement et jusqu'à la 35ème fraction ($\gamma = 0{,}315$) pour le deuxième fractionnement] précipitait dans les tubes du collecteur automatique qui se trouvaient à une température inférieure à celle de la base de la colonne et décantait spontanément. Ceci nous a permis de séparer des sous-fractions pour lesquelles nous avons trouvé des compositions chimiques et des indices de viscosité différents (voir Tableau V). En revanche, les fractions suivantes formaient des suspensions stables au refroidissement. Un phénomène analogue avait été observé lors du fractionnement par précipitation (voir ci-dessus). Il semble être lié à un

caractère particulier du copolymère greffé étudié ici. Une interprétation possible de ce phénomène est donnée plus loin.

Par ailleurs, nous avons constaté au cours de ces fractionnements un "colmatage" de la colonne. En effet, après la 12ème fraction, dans le cas du premier fractionnement ($\gamma = 0{,}680$) et après la 22ème fraction dans le cas du deuxième fractionnement ($\gamma = 0{,}510$), l'écoulement au bas de la colonne s'est brusquement ralenti. Nous avons été obligés de relever le flacon de Mariotte pour maintenir le débit aussi constant que possible; puis l'écoulement s'est accéléré et nous avons pu remettre le flacon d'alimentation à sa position primitive. Il est difficile d'expliquer ce phénomène pour le moment. Il n'est pas exclu qu' avant de se dissoudre, le polymère déposé sur les billes de verre gonfle sous l'effet de l'enrichissement de l'éluant en bon solvant et que ce processus bouche les "interstices" de la colonne. Ce phénomène peut perturber la bonne marche du fractionnement. Il est

TABLEAU IV

Premier Fractionnement par Elution Fractionnée sur Colonne
Copolymère D: $\bar{X} = 80\%$ de Styrène, $[\eta] = 52{,}5$, $\bar{M}_n = 78.300$

Fraction No.	γ	Poids de la fraction, g	$\bar{X}$, % styrène	$[\eta]$ benzène	Observations
1–9	0,930–0,820	0,0025	69,8	—	Solution claire
10	0,764	0,0014	—	—	"
11	0,725	0,0027	—	—	Opalescente
12	0,680	0,0045	—	—	"
13	0,650	0,0067	—	—	"
14	0,600	0,0079	87,4	—	Très opalescente
15	0,560	0,0134	72,7	10	"
16	0,520	0,0191	50,4–49,5	—	"
17	0,470	0,0241	51,8	17,1	"
18	0,430	0,0410	38,9	—	"
19	0,395	0,0295	35,6	—	Décantation
20	0,367	0,0884	73,5	43	"
21	0,345	0,2746	83,0	41	"
22	0,325	0,2629	85,2	59,5	"
23	0,307	0,3426	87,9	54,5	Suspension stable
24	0,290	0,3274	82,2	—	"
25	0,280	0,2401	84,8	—	"
26	0,265	0,1898	85,0	52,5	"
27	0,247	0,08067	94,6	—	"
28	0,236	0,0753	99,5	—	"
29	0,220	0,0617	94,0	—	Très opalescente
30	0,214	0,0502	83,6	53	"
31	0,198	0,0345	74,7	—	"
32	0,187	0,0190	64,7	—	Opalescente
33	0,178	0,0100	68,3	—	"
34	0,169	0,0027	67,9	—	"
35	0,162	0,0025	39,6	—	Claire
36	0,155	0,0022	36,1	—	"
37	0,149	0,0031	26,6	—	"

peut-être la cause de l'obtention des fractions imparfaites qui se séparent spontanément en deux phases au moment du refroidissement (voir ci-dessus).

TABLEAU V

Deuxième Fractionnement par Elution Fractionnée sur Colonne
Copolymère D: X = 80% de Styrène, $[\eta]$ = 52,5, $\bar{M}_n$ = 78.300

Fraction No.	γ	Poids de la fraction g	X, % styrène	$[\eta]$ benzène	$[\eta]$ $CHCl_3$	M_n benzène	Observations
1–12	0,930–0,740	0,0163					Solution claire
13	0,715	0,0011	74,3				"
14	0,695	0,0017					Opalescente
15	0,670	0,0014	94,3				"
16	0,650	0,0021	71,6				"
17	0,615	0,0028	83,8				"
18	0,590	0,0029	82,4				"
19	0,568	0,0038	83,3				"
20	0,548	0,0038					"
21	0,530	0,0055	69,7				Très opalescente
22	0,510	0,0070	62,9	6,7			"
23	0,492	0,0056					"
24	0,475	0,0093	62,1	9	7		"
25	0,456	0,0097	63,3	14,5	10,5		"
26	0,445	0,0132	54,8	23–19	10,5		"
27	0,425	0,0164	54,6	9	17,5		Décantation
28	0,410	0,0157	56,1	25–23	9,5		"
29	0,397	0,0187	50,2	17	20	33.200	"
30	0,385	0,0240	49,3	14	25		"
31	0,370	0,0168	53,4	19,2	25		"
32	0,355	0,0143	64,3	22	26,1		"
33	0,340	0,0499	71,2	24,7	25,5	43.400	"
34 précipité	0,325	0,0987	78,5	43			"
34 solution		0,0088	68,0	30,5	39,1	73.300	"
35 précipité	0,315	0,2360	87,0	52,0			"
35 solution		0,0059	65,7	35,8	57,0	85.200	"
36[a]	0,300	0,2211	87,6	57,0	63,0	104.000	"
37	0,290	0,2119	85,5	58,3	55,0	110.000	Suspension stable
38	0,280	0,1740	97,0	56,8		123.000	"
39	0,270	0,1557	91,0	54,2	63,5	113.000	"
40	0,260	0,1637	91,9	56,5	65,6	119.000	"
41	0,255	0,1223	88,3	58	51,0	107.000	"
42	0,245	0,0960	89,6	57,8	64,0	104.000	"
43	0,240	0,0757	88,5	55	60,5		"
44	0,232	0,0591	86,4	58,5	73,0	111.000	"
45	0,225	0,0449	85,6	59,5	68,8		Tres opalescente
46	0,220	0,0414	85,6	58	68,0		"
47	0,215	0,0313	81,3	40,9	59,4		"
48	0,210	0,0213	83,7	52			"
49	0,205	0,0165	90,5		61,9		Opalescente
50	0,200	0,0143	87,0	57			"

[a] Pour cette fraction, on a trouvé: $\bar{M}_w$ = 138.000 $\bar{M}_w/\bar{M}_n$ = 1,33.

Les deux fractionnements étaient concordants dans leur ensemble; les Tableaux IV et V résument ces résultats.

IV. CARACTERISTIQUES DES FRACTIONS

Nous avons déterminé la composition chimique des différentes fractions obtenues par l'une et l'autre méthode. Sur certaines fractions, nous avons déterminé en outre les indices de viscosité limite dans le benzène et le chloroforme, les masses moléculaires en nombre et en poids par les méthodes précédemment décrites.

Les Tableaux I, II, IV et V résument tous les résultats expérimentaux.

V. DISCUSSION

A. Comparaison des Deux Méthodes de Fractionnement

La méthode classique de fractionnement par précipitation est longue et laborieuse et il est difficile de séparer les polymères ayant de très petits poids moléculaires qui restent en solution en fin d'opération. Pour ces mêmes raison, le nombre total des fractions séparées est généralement assez petit. Dans le présent travail, cette méthode nous a permis cependant d'obtenir un certain nombre de fractions pratiquement monodispersées en poids moléculaires comme le montrent les rapports $\bar{M}_w/\bar{M}_n$ voisins de l'unité (voir par exemple les fractions F3 et F4 dans le Tableau II).

L'élution fractionnée sur colonne est une méthode plus rapide, tout au moins lorsque le fonctionnement de la colonne de fractionnement a été correctement mis au point. On peut obtenir par cette méthode un très grand nombre de fractions, mais la qualité du fractionnement dépend dans une large mesure d'un grand nombre de facteurs liés à la marche de l'appareil. Dans notre cas, nous avons des indications que le fractionnement n'était pas rigoureux, tout au moins dans un certain domaine de solubilités (voir plus loin). De plus, le colmatage de la colonne observé dans certaines conditions peut perturber la bonne marche du fractionnement.

Nous pensons que les deux méthodes peuvent être considérées comme complémentaires pendant la période de mise au point définitive de la méthode par élution fractionnée mais que cette dernière méthode est à préférer ensuite.

La plupart des renseignements obtenus dans le présent travail par les deux méthodes sont en bon accord, bien que des différences significatives soient apparues dans certains cas. Il est à noter que les deux précipitants employés: *n*-propanol et isopropanol ont donné des γ de précipitation assez concordants.

B. Caractrisétiques des Fractions

L'examen des données présentées dans les Tableaux I, II, IV et V fait ressortir une évolution assez complexe des caractéristiques des fractions. Celle-ci est particulièrement frappante si l'on considère la variation de la

composition chimique avec l'ordre de la fraction. Les courbes 1 des Figures 3 et 4 représentent graphiquement la variation de la composition $\bar{X}$ des fractions en fonction du poids cumulé. On voit en effet que la composition varie très peu pour les fractions à poids moléculaire élevé, obtenues à des γ compris entre 0,150 et 0,300. Nous trouvons une relation analogue pour les fractions obtenues par les deux méthodes de fractionnement. L'ensemble de ces fractions représente environ 70% du poids total du polymère. On peut donc en conclure que la plus grande partie du copolymère greffé possède une distribution en compositions assez étroite. Remarquons par ailleurs que toutes ces fractions précipitent (ou sont éluées) dans un domaine de γ assez étroit. Ces mêmes fractions présentent la particularité de former des suspensions stables qui ne décantent pas spontanément même après plusieurs jours de repos (voir plus haut).

Pour les fractions séparées à des γ supérieurs à 0,300, la teneur en styrène tombe brusquement. Les fractions ainsi obtenues ont un comportement assez différent des fractions précédentes. En particulier, elles se séparent très facilement par décantation spontanée.

Enfin, pour des γ supérieurs à 0,400 environ, on obtient des fractions dont la teneur en styrène augmente à nouveau et semble tendre vers 100%. Seule la méthode de fractionnement par élution a permis d'isoler ces fractions (les plus solubles).

Les indices de viscosité limite évoluent d'une façon qui rappelle dans une certaine mesure l'évolution des compositions. Une différence significative apparaît ici entre les fractions obtenues par les deux méthodes. En les indices de viscosité limite des fractions isolées par précipitation fractionnée décroissent régulièrement avec le numéro de la fraction. Notons cependant que l'indice de viscosité de la dernière fraction isolée (F_6)

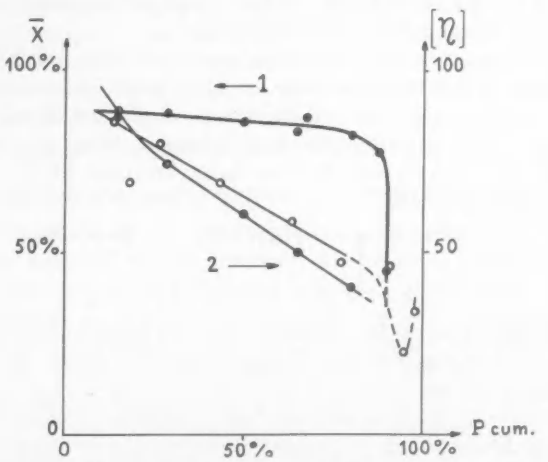


Fig. 3. Variation de la composition chimique (*1*) de l'indice de viscosité limite et (*2*) en fonction du poids cumulé: (●) copolymère H; (○) copolymère K.

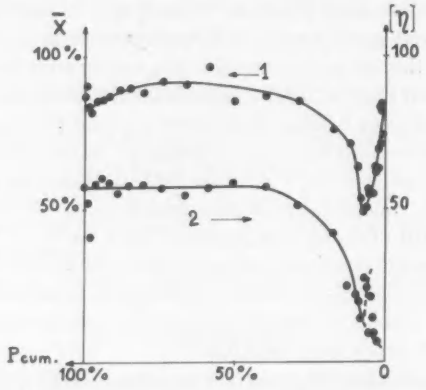
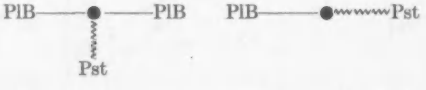


Fig. 4. Variation de la composition chimique (*1*) de l'indice de viscosité limite et (*2*) en fonction du poids cumulé pour le copolymère D.

augmente à nouveau. La méthode de fractionnement par élution a donné des fractions dont les indices de viscosité limite sont sensiblement constants dans le domaine où les compositions sont constantes. Ce résultat pourrait indiquer que le fractionnement n'est pas très éfficace pour ces polymères. Une chute de la viscosité se produit en même temps qu'une chute de la teneur en styrène dans les fractions; enfin, pour les fractions les plus solubles, l'indice de viscosité limite tend à augmenter en même temps que la teneur en styrène (courbes *2* des Figures 3 et 4).

Nos données sur les masses moléculaires $\bar{M}_n$ et $\bar{M}_w$ des fractions sont encore trop fragmentaires pour permettre de vérifier ou d'infirmer l'existence d'un minimum analogue. Il faut remarquer en outre que les poids moléculaires de ces fractions sont très petits.

L'interprétation de cette évolution complexe nous paraît prématurée. Notre hypothèse de travail actuelle est la suivante. Admettons pour fixer les idées que les fractions soient constituées de chaînes de polyisobutylène portant une seule branche greffée de polystyrène. Selon que cette branche est greffée latéralement ou en bout de chaîne, on aurait ainsi l'une ou l'autre des structures suivantes:



Considérons d'abord les fractions ayant les poids moléculaires les plue élevés, nous pouvons dire selon l'image proposée ci-dessus, que la tendance à la diminution simultanée de la viscosité et de la teneur en styrène, observée dans les fractions obtenues par précipitation fractionnée, doit être due à une diminution de la longueur de la branche greffée de polystyrène. Les longueurs des chaînes de polyisobutylène de ces fractions doivent rester constantes en moyenne. En effet, le polyisobutylène étant entièrement

soluble dans ce domaine de γ (γ de précipitation à 25°C du polyisobutylène = 0,332 dans le propanol et = 0,345 dans l'isopropanol), il est peu probable qu'il puisse se fractionner dans ces conditions. La chute brutale de la teneur en styrène dans les fractions obtenues, entre $\gamma = 0{,}300$ et $\gamma = 0{,}400$, par les deux méthodes, correspondrait à une diminution brutale de la longueur des branches greffées. Au minimum de la courbe 1 de la Figure 4, la masse moléculaire $\bar{M}_n$ est égale à 33.200 (fractions 29 et 30 du Tableau V) pour une composition voisine de 50% en styrène. Cela signifie que la longueur des branches de styrène dans ces fractions est au plus égale à 16.600.

Le minimum aigu sur la courbe *1* de la Figure 4 et l'augmentation de la teneur en styrène observée pour les fractions les plus solubles suggèrent que, dans ce domaine de γ ($\gamma = 0{,}400$ à $\gamma = 0{,}930$), c'est la longueur des chaînes de polyisobutylène qui diminue progressivement dans les fraction. La longeur des branches greffés de polystyrène doit être très petite. En effet, seules des branches de polystyrène extrêmement courtes peuvent rester en solution dans ces mélanges très riches en précipitant, et par conséquent, ce sont le chaînes de polyisobutylène qui doivent être fractionnées le plus efficacement. Les fractions les plus solubles seraient donc constituées de branches de polystyrène qui ne renferment qu'un petit nombre de motifs monomères (inférieur à 100 environ d'après les indices de viscosité limite) attachés à des fragments très petits de polyisobutylène.

L'image proposée permet d'expliquer le comportement des différentes fractions dans un mauvais solvant. En effet, pour les γ compris entre 0,150 et 0,300 seules les branches de polystyrène précipitent; les chaînes de polyisobutylène restent déployées et solubilisent l'ensemble de la molécule. On obtient ainsi des suspensions stables. Dans la région du minimum des teneurs en styrène (γ compris entre 0,330 et 0,425), les deux types de polymères précipitent et le copolymére greffé décante spontanément. Enfin, pour les fractions les plus solubles, ce sont les chaînes de polyisobutylène qui ont tendance à précipiter les premières et elles restent solubilisées par les branches très courtes de polystyrène. Nous avons effectivement observé des solutions opalescentes en laissant refroidir ces fractions.

C. Conséquences pour la Structure du Copolymère Greffé

La discussion précédente, qui est basée sur des résultats encore fragmentaires, semble indiquer que la distribution en masses moléculaires des branches de polystyrène greffé n'est pas régulière. Il existerait une proportion significative de branches extrèmement courtes. Celles-ci seraient responsables des anomalies observées pour les compositions chimiques et les viscosités des fractions les plus solubles. La formation de branches de polystyrène très courtes peut s'expliquer par les conditions particulières dans lesquelles s'effectue la réaction de greffage (milieu précipitant, séparation en deux phases et coalescence des chaînes croissantes.[6] Remarquons que les fractions renfermant ces branches courtes ne représentent en tout que 10% environ du copolymère total.

Nous espérons vérifier les différentes hypothèses émises au cours de ce travail lorsque de nouvelles données expérimentales seront obtenues. Des études dans ce sens sont actuellement en cours.

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Résumé

Le copolymère greffé utilisé avait été préalablement séparé des deux homopolymères correspondants per extraction sélective. Deux méthodes ont été utilisées pour le fractionnement proprement dit. (*1*) Une précipitation fractionnée par le propanol, à partir d'une solution du copolymère dans le cyclohexane. Cette méthode a permis d'obtenir une dizaine de fractions à partir d'échantillons de 1 à 5 g. de copolymère. Les fractions ont été caractérisées par leurs compositions chimiques, leurs indices de viscosité limite et leurs masses moléculaires moyennes ($\bar{M}_n$ par osmométrie et $\bar{M}_w$ par diffusion de la lumière). (*2*) Une élution fractionnée selon la méthode de Baker et Williams sur une colonne possédant un gradient linéaire de températures et un gradient de compositions en éluant (couple isopropanol–cyclohexane). En partant de 2 g. de copolymère, on a obtenu une quarantaine de fractions dont on a déterminé les compositions chimiques, les indices de viscosité limite et, pour certaines d'entre elles, les masses moléculaires moyennes en nombre par osmométrie. L'isolement des fractions obtenues par la précipitation fractionnée a été sérieusement compliqué par le fait que, dans un grand domaine de γ de précipitation (rapport du volume de précipitant au volume total), les copolymères ne se décantaient pas spontanément: il fallait alors recourir à une centrifugation. Pour les denières fractions (les plus riches en isobutylène), la séparation se faisait spontanément par floculation. Un phénomène analogue a été observé lors du fractionnement par élution: parmi les premières fractions collectées, les plus riches en isobutylène, précipitaient spontanément au refroidissement, tandis que les fractions ultérieures, les plus riches en styrène formaient des suspensions stables. La variation des compositions chimiques en fonction de l'ordre de la fraction a été étudiée. Les fractions correspondant aux masses moléculaires les plus élevées ont une composition chimique sensiblement constante, comprenant 85–90% de styrène. A partir d'un γ de précipitation bien déterminé, la teneur en styrène décroît brusquement et atteint 40–50%. Pour les fractions ayant les plus petites masses moléculaires (seulement obtenues par l'élution fractionnée), la teneur en styrène croît de nouveau et atteint 85–90%. Il est intéressant de

noter que le phénomène de floculation des fractions apparaît précisément lorsque la teneur en styrène commence à décroître. La variation des indices de viscosité limite des fractions, obtenues par l'une ou l'autre méthode, a été étudiée en fonction de l'ordre de la fraction. Certaines anomalies apparaissent dans cette étude. Il en est de même pour les masses moléculaires en nombre et pour les masses apparentes en poids. L'ensemble de ces résultats est discuté et on en déduit en particulier des conséquences sur la structure du copolymère greffé.

Synopsis

The graft copolymer was previously separated from the both corresponding homopolymers by selective extraction. Two methods have been used for the fractionation: (*1*) Fractionation by precipitation of the copolymer solution in cyclohexane with propanol. This method makes it possible to obtain ten fractions starting from 1–5 g. copolymer. These fractions were characterized by their chemical compositions, limited viscosity number, mean molecular weights ($\bar{M}_n$ by osmometry and $\bar{M}_w$ by light scattering). (*2*) Fractionation by elution following the method of Baker and Williams by means of a column with a linear temperature gradient and a eluent composition gradient: (isopropanolcyclohexane system). Starting from 2 g. of copolymer, forty fractions were obtained of which the chemical composition, the limited viscosity number and, for some of them, the number average molecular weight, as determined by osmometry. The isolation of the fractions obtained by precipitation was quite complicated: indeed, over a broad domain of gamma-valves (volume fraction of precipitant) the copolymers did not precipitate spontaneously; it was then necessary to carry out centrifugation. For the last fractions (with highest isobutene content) the separation proceeded spontaneously by flocculation. A similar phenomenon was observed during the fractionation by elution: between the first collected fractions, those richest in isobutene precipitated spontaneously on cooling, while the following fractions (richest in styrene) formed stable suspensions. The variation of chemical composition of each fraction has been studied. The fractions with highest molecular weights have a sensibly constant chemical composition, varying between 85 and 90% styrene. From a well-determined gamma-valve, the styrene content decreases abruptly and is equal to 40–50%. For the fractions with lowest molecular weights (only obtained by elution fractionation), the styrene content increases again and attains 85–90%. It is interesting to notice that the floculation phenomenon of the fractions appears precisely when the styrene content begins to decrease. The variation of limited viscosity numbers of the fractions, obtained by one of the two methods has been studied in function of the number of the fraction. Some anomalies becomes apparent in this study, as well as for the average number molecular weights and the apparent average weight molecular weights. These results were discussed and their consequences deduced in relation with the structure of the graft copolymer.

Zusammenfassung

Das verwendete Pfropfcopolymere wurde durch selektive Extraktion von den beiden entsprechenden Homopolymeren getrennt. Für die eigentliche Fraktionierung kamen zwei Methoden zur Anwendung. (*1*) Eine fraktionierte Fällung des Copolymeren in Cyclohexanlösung mit Propanol. Diese Methode hat die Gewinnung von etwa 10 Fraktionen aus 1 bis 5 g-Proben des Copolymeren ermöglicht. Die Fraktionen wurden durch ihre chemische Zusammensetzung, ihre Grenzviskositätszahlen und mittleren Molekulargewichte ($\bar{M}_n$ osmometrisch und $\bar{M}_w$ durch Lichtstreuung) charakterisiert. (*2*) Eine fraktionierte Eluierung nach Baker und Williams an einer Säule mit linearem Temperaturgradienten und einem Zusammensetzungsgradienten des Eluierungsmittels (Isopropanol-Cycylohexan). Ausgehend von 2 g Copolymerem wurden etwa 40 Fraktionen erhalten, deren chemische Zusammensetzung, Grenzviskositätszahl und, in einigen Fällen, Zahlenmittel des Molekulargewichts (osmometrisch) bestimmt wurden. Die

Isolierung der durch fraktionierte Fällung erhaltenen Fraktionen wurde dadurch sehr erschwert, dass sich die Copolymeren in einem grossen Fällungsbereich (Vdrhältnis von Fällungsmittelvolumen zu Gesamtvolumen) nicht spontan absetzten, sondern eine Zentrifugierung durchgeführt werden musste. Bei den letzten Fraktionen (den Isobutylenreichsten) trat spontane Trennung durch Ausflockung ein. Eine analoge Erscheinung wurde dann bei der Eluierungsfraktionierung beobachtet. Unter den zuerst aufgefangenen Fraktionen flockten die Isobutylenreichsten beim Abkühlen spontan aus, während die späteren Fraktionen (die Styrol-reicheren) stabile Suspensionen bildeten. Die Änderung der chemischen Zusammensetzung im Verlauf der Fraktionierung wurde untersucht. Die Fraktionen mit den höchsten Molekulargewichten besitzen eine im wesentlichen konstante chemische Zusammensetzung mit 85 bis 90% Styrol. Bei einem wohldefinierten Fällungsgrad fällt der Styrolgehalt plötzlich ab und erreicht 40 bis 50%. Bei den Fraktionen mit dem kleinstein Molekulargewichten (nur durch fraktionierte Eluierung erhalten) nimmt der Styrolgehalt wieder zu und erreicht 85 bis 90%. Interessanterweise tritt die Ausflockung der Fraktionen genau bei beginnender Abnahme des Styrolgehaltes auf. Die Änderung der Grenzviskositätszahlen der nach der einen oder anderen Methode erhaltenen Fraktionen im Verlauf der Fraktionierung wurde untersucht. Dabei treten gewisse Anomalien auf. Das gleiche gilt für das Zahlen- und Gewichtsmittel des Molekulargewichts, Die Ergebnisse werden in ihrer Gesamtheit diskutiert und Folgerungen auf die Struktur des Pfropfcopolymeren gezogen.

Discussion

Ch. Cousin (*Ethylene Plastique, Mazingarbe, France*): Avez-vous tenté de refractionner par élution des fractions obtenues par précipitation?

P. Cordier: Nous n'avons pas encore réalisé ce genre d'experiences. Elles compléteraient les résultats que nous avons obtenus par les deux méthodes exposées dans la présente communication.

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Configuration des Chaînes Macromoléculaires des Copolymères Sequences en Solution Concentree. Exemple des Copolymères Séquencés Polystyrolène–Polyoxyéthyléne et Polyoxypropylène–Polyoxyéthylène en Solution dans des Solvants Préférentiels de l'une ou l'autre des Séquencés

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INTRODUCTION

L'une des propriétés les plus caractéristiques des savons est leur aptitude à fournir, quand ils sont mis en présence de solvants convenablement choisis, des phases mésomorphes, ayant l'aspect de gels translucides et présentant une biréfringence optique spontanée.[1] Cette propriété est étroitement liée au caractère amphipathique des savons qui contiennent, dans leur molécule, deux parties distinctes, l'une hydrophile, l'autre hydrophobe, et douées d'une assez grande indépendance réciproque.

Nous avons récemment effectué une étude systématique de la structure des gels mésomorphes de savon; nous avons, en particulier, examiné le cas des savons purs,[2] des mélanges savon–eau,[3] savon–hydrocarbure,[4] savon–eau–hydrocarbure.[5] Parmi les structures que nous avons établies, mentionnons les structures à feuillets, à cylindres, à sphères et à rubans qui sont les plus représentatives. Leur caractéristique commune et essentielle réside dans l'indépendance des deux parties des molécules de savon qui occupent, dans la matière, des régions distinctes et juxtaposées, en y conservant leur entière individualité. Les chaînes paraffiniques ont une configuration désordonnée, alors que les groupes polaires en absence de solvant polaire, sont "cristallisés." En ce qui concerne le solvant contenu dans le système, il est localisé parmi les chaînes paraffiniques, quand il s'agit d'un hydrocarbure, et dans les régions occupées par les groupes polaires, quand c'est de l'eau.

En partant de ces résultats, nous nous sommes demandés si la notion de caractère amphipathique, de dissolution partielle des molécules et de formation de phases mésomorphes, observée pour les savons, est également valable dans le domaine macromoléculaire. Il nous a en effet semblé légitime de penser qu'une macromolécule, telle un copolymère séquencé,

a un comportement analogue à celui des savons: mise en présence d'un bon solvant de l'un des deux types de séquences et précipitant de l'autre, elle adopte une configuration qui respecte la dissolution dans le solvant des séquences solubles et la précipitation, sur elles-mêmes, des séquences insolubles. En opérant dans des solutions concentrées, où sont favorisées les interactions entre chaînes de polymère, il nous a en outre paru légitime d'espérer obtenir des phases mésomorphes, similaires à celles que l'on obtient dans les solutions concentrées de savon.

Afin de vérifier ce point de vue, nous avons entrepris l'étude des solutions concentrées de copolymères séquencés dans des solvants préférentiels de l'un des deux types de séquences.[7-9] Parmi les copolymères séquences dont nous disposions, nous avons choisi les copolymères polystyrolène–polyoxyéthylène et polyoxypropylène–polyoxyéthylène qui ont une constitution chimique similaire à celle des savons et qui de ce fait nous ont paru le mieux adaptés à une étude systématique d'exploration. (Quelques essais rapides nous ont néanmoins montré que les conclusions relatives à ces deux copolymères s'appliquent non seulement à d'autres copolymères séquencés, mais également à des copolymères greffés.) Les séquences qu'ils comportent ont en effet des propriétés très différentes: les séquences polystyrolène et polyoxypropylène sont hydrophobes et les séquences polyoxyéthylène hydrophiles; de plus, leurs solutions aqueuses moussent abondamment par simple agitation et, additionnées d'un liquide organique insoluble dans l'eau, conduisent à l'image des savons, à des émulsions relativement stables.[6] Nous avons ainsi réussi à obtenir des phases mésomorphes et, en examinant leur structure à l'aide de la diffraction des rayons X, à retrouver les structures à feuillets, à cylindres ou à sphères rencontrées dans les gels de savon.

Sans présenter les arguments qui nous ont permis d'établir ces structures,[8-9] nous nous contenterons d'en décrire, dans le présent mémoire, quelques exemples caractéristiques, dont nous exposerons les propriétés principales et dont nous nous servirons pour discuter la configuration des chaînes macromoléculaires des copolymères séquencés en solution concentrée.

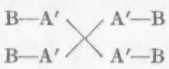
PARTIE EXPERIMENTALE

Produits Utilisés

Les exemples de structures que nous présenterons dans le chapitre suivant concernent trois copolymères séquencés, désignés respectivement par 503C, Tétronic 904 et Pluronic 66. Le premier de ces copolymères a été préparé dans notre laboratoire;[10] les deux autres nous ont été aimablement fournis par la Société Wyandotte (U.S.A).

Le copolymère 503C est un copolymère linéaire, formé d'une séquence A centrale de polystyrolène (PS) entourée de deux séquences B de polyoxyéthylène (POE). Sa structure chimique schématisée est B—A—B.

Le copolymère Tétronic 904 est un copolymère cruciforme, formé de quatre séquences A′ de polyoxypropylène (POP) reliées à une molécule centrale d'éthylènediamine et prolongées, chacune, d'une séquence B de polyoxyéthylène (POE). Sa structure chimique schématisée est



Le copolymère Pluronic 66 est un copolymère linéaire, formé d'une séquence A′ centrale de polyoxypropylène (POP) entourée de deux séquences B de polyoxyéthylène (POE). Sa structure chimique schématisée est B—A′—B.

Nous avons vérifié que ces copolymères ne contiennent pas de quantités appréciables d'homopolymère. Nous avons groupé leurs charactéristiques physicochimiques dans le Tableau I: X_A, $X_{A'}$, et X_B représentent respec-

TABLEAU I

Désignation	Type	X_A(ou $X_{A'}$)	X_B	M_A(ou $M_{A'}$)	M_B	M
503C	B—A—B	0,54	0,46	16.100	13.800	29.900
Tétronic 904	B—A′ X A′—B B—A′ X A′—B	0,49	0,51	2.000	2.100	4.100
Pluronic 66	B—A—B	0,68	0,32	4.400	2.100	6.500

tivement les teneurs en polystyrolène, polyoxypropylène et polyoxyéthylène; M_A, $M_{A'}$, et M_B les masses moléculaires en nombre des parties A, A′, et B; M les masses moléculaires en nombre globales ($M = M_A + M_B$; $M = M_{A'} + M_B$).*

Comme solvants préférentiels du POE, nous avons utilisé le nitrométhane qui est un précipitant du PS et l'eau qui est un précipitant du POP; comme solvant préférentiel du PS, nous avons employé le phtalate de butyle qui est un précipitant du POE; et comme solvant préférentiel du POP, nous avons utilisé le nitrobenzène qui, sans être un précipitant du POE, dissout mieux le POP que le POE.

Préparation des Solutions

Nous avons préparé les solutions par pesée directe des quantités calculées de copolymère et de solvant. Après homogénéisation prolongée (48 heures), par chauffage à une température de 20°C inférieure à la température d'ébullition du solvant, et refroidissement lent (12 heures), nous laissions les solutions séjourner à température ordinaire pendant une semaine au moins. Ce traitement nous a paru suffisant pour atteindre l'équilibre thermodynamique des solutions.

* Pour évaluer les masses moléculaires en nombre, nous nous sommes fondés sur ce que l'on sait de la polydispersité des polymères obtenus par polycondensation d'époxydes, et nous avons admis que la masse moléculaire en poids déterminée par diffusion de la lumière est égale au produit de la masse moléculaire en nombre par 1,2.

Techniques Expérimentales

Nous avons fait appel à deux techniques expérimentales, microscopie en lumière polarisée et diffraction des rayons X, déjà utilisées dans l'étude des savons.[3] Nous ne les décrirons pas ici.

RESULTATS ET DISCUSSION

En examinant au microscope polarisant les solutions concentrées des copolymères séquencés dans des solvants préférentiels de l'une des séquences, nous avons pu identifier un certain nombre de phases spontanément anisotropes; nous avons également pu reconnaître, pour chacune d'elles, un type bien déterminé de textures.[7,8]. L'examen aux rayons X de ces phases a conduit à la description de trois familles de structures: à feuillets, à cylindres et à sphères.[7,8] Nous allons les passer en revue, sans insister sur la manière dont nous avons pu les établir. Nous nous référons, pour l'étude cristallographique détaillée de ces phases, aux mémoires que nous avons déjà publiés ailleurs.[8,9]

Structure à Feuillets

Nous avons rencontré cette structure dans les copolymères purs, ainsi que dans leurs mélanges avec un solvant; et notamment dans les mélanges du Tétronic 904 avec l'eau, du Pluronic 66 avec le nitrobenzène et du copolymère 503C avec le phtalate de butyle, pour des teneurs en copolymère comprises respectivement entre 75 et 100%, entre 70 et 100%, et entre 50 et 100%.

Le modèle que nous avons adopté pour cette structure[7,8] correspond à l'empilement périodique de feuillets plans et indéfinis. Chaque feuillet est constitué par la superposition de deux couches, l'une contenant les séquences incompatibles avec le solvant, l'autre le mélange intime des séquences solubles avec le solvant. Dans le cas des mélanges avec l'eau, le solvant est localisé parmi les séquences POE; dans le cas des mélanges avec le phtalate de butyle ou le nitrobenzène, le solvant est localisé parmi les séquences PS ou POP.

Quant aux chaînes macromoléculaires engagées dans la structure à feuillets, si les séquences PS et POP sont, dans tous les cas étudiés, désordonnées comme dans un échantillon amorphe, la configuration des séquences POE, elle, dépend de la nature du solvant présent dans le système. En présence d'eau, qui dissout le POE, ces séquences adoptent la configuration chaotique d'un échantillon amorphe; au contraire, en présence de phtalate de butyle ou de nitrobenzène, qui dissolvent mal le POE, ces séquences sont "cristallisées."

Nous avons caractérisé la structure à feuillets par trois paramètres:[8,9] l'épaisseur d d'un feuillet élémentaire, égale à la somme des épaisseurs des deux couches qui le constituent, l'épaisseur d_f d'une couche contenant les séquences incompatibles avec le solvant présent dans le système, et la surface spécifique s qui représente la surface disponible, au niveau

TABLEAU II

Système	c, %	d, A	d_i, A	s, A^2
Copolymère 503C + phtalate de butyle	50	366	81	249
	60	318	84	240
	70	272	84	240
	79	234	80	252
	88	205	80	252
Tétronic 904 + eau	74	85	44	68
	76	83	44	69
	81	80	45	67
	85	79	47	65
	90	74	47	65
	95	71	48	64
	100	212	152	22
Pluronic 66 + nitrobenzène	80	251	91	28
	90	232	96	27
	100	220	115	25

de la surface de séparation entre couches, pour un point de jonction de deux séquences différentes dans une macromolécule (Tableau II, Figs. 1-3).

S'il est aisé de discuter l'évolution de l'épaisseur d des feuillets en fonction de la concentration et d'attribuer son augmentation avec la teneur en solvant au gonflement de l'édifice dû à la croissance de l'épaisseur des couches contenant les séquences solubles, il est plus délicat, par contre, d'étudier la variation de l'épaisseur d_i des couches contenant les séquences insolubles. Il faut pour cela considérer séparément le cas où les séquences POE sont désordonnées et le cas où celles-ci sont "cristallisées."

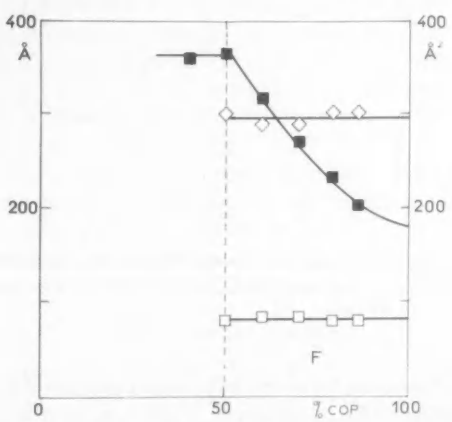


Fig. 1. Paramètres structuraux du système copolymère 503C–phtalate de butyle: (■) épaisseur du feuillet élémentaire; (□) épaisseur de la couche POE; (◇) surface spécifique. Domaines d'existence: *F*, feuillets.

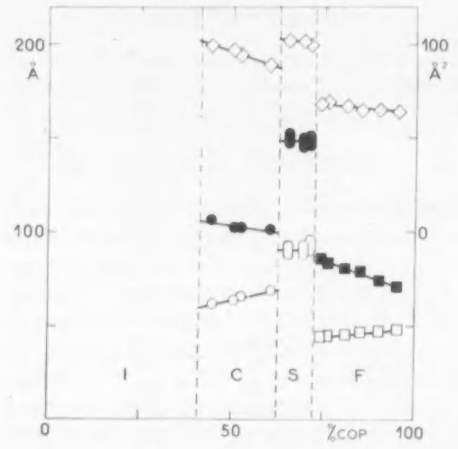


Fig. 2. Paramètres structuraux du système Tétronic 904–eau: (■) épaisseur du feuillet élémentaire; (□) épaisseur de la couche POP; (▮) côté de la maille cubique; (▯) diamètre des sphères; (●) distance entre les axes de deux cylindres voisins; (○) diamètre des cylindres; (◇) surface spécifique. Domaines d'existence: *I*, solution isotrope; *C*, cylindres; *S*, sphères; *F*, feuillets.

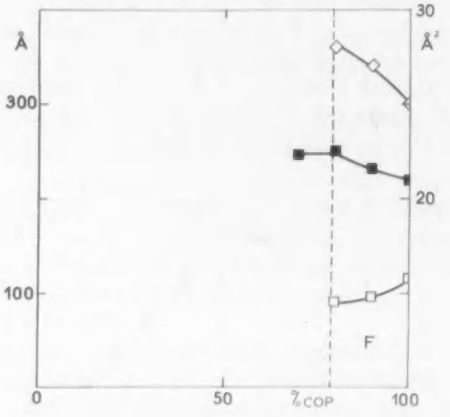


Fig. 3. Paramètres structuraux du système Pluronic 66–nitrobenzène: (■) épaisseur du feuillet élémentaire; (□) épaisseur de la couche POP; (◇) surface spécifique. Domaines d'existence: *F*, feuillets.

Lorsque tous les deux types de séquences présentés dans le copolymère adoptent la configuration désordonnée (c'est le cas pour le système Tétronic 904–eau), l'épaisseur d_t diminue, et conjointement la surface spécifique augmente, quand la teneur en solvant croît (Fig. 2). Ce phénomène est en relation avec les interactions entre les séquences POE et l'eau qui

perturbent la configuration de ces séquences, et par répercussion, la configuration des séquences insolubles.

Lorsque les séquences POE sont "cristallisées" (c'est le cas pour le système copolymère 503C-phtalate de butyle), l'épaisseur d_t, et conjointement la surface spécifique, restent constantes (Fig. 1). Ceci indique que les interactions PS–phtalate de butyle sont insuffisamment intenses pour modifier la configuration des séquences PS qui, par ailleurs, se trouvent ancrées sur les séquences POE "cristallisées." Il convient cependant d'opposer à ce cas idéal, celui du système Pluronic 66–nitrobenzène où les séquences POE sont également "cristallisées," mais où d_t diminue quand la teneur en solvant augmente (Fig. 3). Rappelons que, dans ce dernier cas, le nitrobenzène n'est pas un précipitant du POE mais uniquement un solvant préférentiel du POP. On peut expliquer la décroissance de d_t en fonction de la concentration, par une dissolution partielle des séquences POE qui entraînerait l'inclinaison progressive des chaînes "cristallisées," et non encore "dissoutes," par rapport au plan des feuillets.

Lorsque nous affirmons que les chaînes POE sont cristallisées, nous entendons qu'elles admettent la même structure[8,9] qu'un échantillon polycristallin d'homopolyoxyéthylène. Or nous savons[11] que dans ce dernier cas le polymère cristallise dans le système monoclinique (a = 9,5 A; b = 19,5 A; c = 12,0 A; β = 101°) et que la maille élémentaire contient 36 unités monomères, groupées en quatre chaînes macromoléculaires dirigées parallèlement au côté b de la maille. Il est facile de montrer que la masse moléculaire qui correspond à une longueur de 1 A de chaîne est alors de 20,3 et que l'encombrement latéral moyen d'une chaîne, dans le plan formé par les côtés a et c de la maille, est de 28 A^2. Si l'on examine maintenant l'épaisseur d_t et la surface spécifique s, en fonction des données relatives au POE cristallin, on constate que, dans le cas du système copolymère 503C–phtalate de butyle, les chaînes POE sont dirigées perpendiculairement au pan des feuillets et sont repliées quatre fois sur elles-mêmes, comme se replient les chaînes macromoléculaires dans les polymères cristallins,[12] le polyéthylène Marlex 50 par exemple. Au contraire, dans le cas du Tétronic 904 pur et Pluronic 66 pur, les chaînes POE sont dirigées perpendiculairement au plan des feuillets, ne sont pas repliées sur elles-mêmes, mais assemblées en double couche.[8] Ce phénomène est en relation avec la masse moléculaire des séquences POE. Pour le copolymère 503C, cette masse est de 6900 alors que pour le Tétronic 904 et Pluronic 66, elle n'est que de l'ordre de 600–1000.

Structure à Cylindres

Nous avons rencontré cette structure dans les mélanges du Tétronic 904 avex l'eau, du Pluronic 66 avec l'eau et du copolymère 503C avec le nitrométhane, pour des teneurs en copolymère comprises respectivement entre 40 et 65%, entre 60 et 95% et entre 50 et 90%.

Le modèle que nous avons adopté pour cette structure est le suivant.[8,9] Des cylindres indéfinis et parallèles, formés, par les séquences du copolymère

qui se trouvent être insolubles dans le solvant présent dans le système, sont disposés aux noeuds d'un réseau bidimensionnel hexagonal. Ils sont séparés les uns des autres par le mélange intime des séquences solubles avec le solvant. Comme, dans le cas des copolymères que nous considérons ici, la structure à cylindres est observée uniquement en présence de solvants du POE, nous pouvons préciser, pour la clarté de l'exposé, que les cylindres sont constitués par les séquences PS et POP, les séquences POE étant localisées dans l'espace intercylindrique. La configuration des chaînes macromoléculaires engagées dans la structure est désordonnée et chaotique.

TABLEAU III

Système	c, %	D, A	D_i, A	s, A^2
Copolymère 503C + nitrométhane	50	251	139	366
	60	236	144	352
	69	219	143	356
	78	226	157	324
	89	212	157	324
Tétronic 904 + eau	44	106	61	99
	50	102	63	97
	52	102	65	94
	60	101	68	89
Pluronic 66 + eau	70	95	59	94
	80	92	62	90
	84	90	63	89
	85	89	62	90
	90	87	62	90
	91	84	61	92

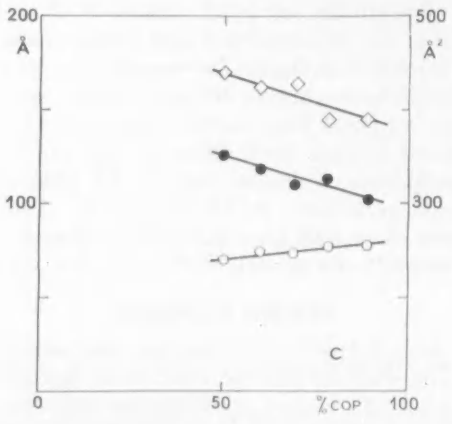


Fig. 4. Paramètres structuraux du système copolymère 503C–nitrométhane: (●) distance entre les axes de deux cylindres voisins; (○) diamètre des cylindres; (◇) surface spécifique. Domaines d'existence: C, cylindres.

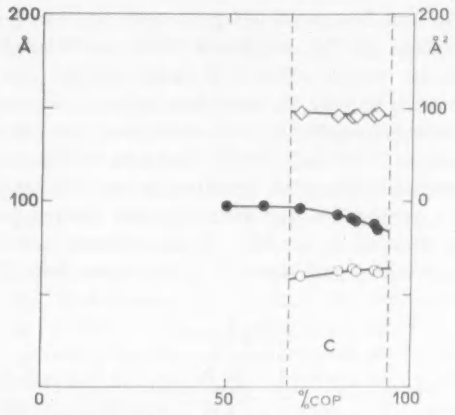


Fig. 5. Paramètres structuraux du système pluronic 66–eau: (●) distance entre les axes de deux cylindres voisins; (○) diamètre des cylindres; (◇) surface spécifique. Domaines d'existence: *C*, cylindres.

Nous avons caractérisé la structure à cylindres par trois paramètres:[3,9] la distance D qui sépare les axes de deux cylindres voisins, le diamètre D_t des cylindres et la surface spécifique s définie comme précédemment (Tableau III, Figs. 2, 4, 5).

Si la distance D augmente régulièrement lorsque la teneur en solvant croît, le mécanisme de gonflement du système n'est pourtant pas simple. On ne peut pas décrire le gonflement comme résultant d'un simple écartement des cylindres et de la localisation du solvant dans l'espace ainsi dégagé, car le diamètre des cylindres ne reste pas constant. Le fait que le diamètre des cylindres décroît lorsque la teneur en solvant augmente, et que, conjointement, la surface spécifique s croît, indique l'existence, entre les séquences solubles et le solvant, d'interactions non négligeables qui perturbent la configuration de ces séquences, et, par répercussion, la configuration des séquences insolubles.

Dans un mémoire précédent,[8] nous avons admis que le diamètre des cylindres, et la surface spécifique, ne dépendent pas de la teneur en solvant, ni même de la masse moléculaire des séquences solubles. Rappelons toutefois qu'il s'agissait là d'une première approximation.

Pour les copolymères contenant des séquences POP, la surface spécifique est voisine de 90 A², alors que pour les copolymères contenant des séquences PS, celle-ci est voisine de 350 A². S'il en est ainsi, c'est que l'encombrement différent des unités monomères du POP et du PS imposent des configurations différentes aux chaînes macromoléculaires, tout au moins au niveau des surfaces des cylindres.

Structure à Sphères

Nous avons rencontré cette structure dans les mélanges du Tétronic 904 avec l'eau, pour des teneurs en copolymère comprises entre 65 et 71%.

Le modèle que nous avons adopté pour cette structure est le suivant. Des sphères, formées par les séquences POP insolubles dans l'eau sont assemblées selon un réseau cubique à faces centrées qui correspond à ce qu'il est convenu d'appeler, en cristallographie, un assemblage compact de sphères. L'espace compris entre les sphères est rempli par le mélange intime des séquences POE avec l'eau. Dans ce modèle, la configuration des chaînes macromoléculaires est désordonnée et chaotique.

Nous avons caractérisé cette structure par quatre paramètres:[9] le côté D la maille cubique, le diamètre D_i des sphères, la surface spécifique s et le nombre n de macromolécules afférentes à une sphère (Tableau IV).

TABLEAU IV

Système	c, %	D, A	D_i, A	s, A^2	n
Tétronic 904 +	65	150	90	102	62
eau	69	147	90	102	62
	71	148	92	100	68

CONCLUSION

En choisissant, parmi les substances macromoléculaires, les copolymères séquencés, dont la constitution chimique rappelle formellement tout au moins, celle des savons, et en faisant usage des notions de caractère amphipathique et de phases mésomorphes mises en avant pour ces derniers, nous avons réussi à obtenir des phases présentant une biréfringence optique spontanée et possédant des structures analogues à celles des phases mésomorphes de savon. Nous avons notamment identifié des structures àfeuillets, à cylindres et à sphères, dont nous avons en outre étudié les paramètres à l'aide de la diffraction des rayons X.

L'examen de ces structures permet d'évaluer l'importance des interactions entre les séquences et le solvant, et entre les séquences elles-mêmes en ce qui concerne la configuration des chaînes macromoléculaires. Cette configuration est éloignée de celle prévue par la statistique de Gauss, au point que les deux types de séquences présentes dans la macromolécule occupent, dans la matière, des régions distinctes et juxtaposées, le solvant pénétrant, au gré de ses affinités, parmi les séquences pour lesquelles il manifeste une plus grande affinité.

L'orientation moyenne des chaînes macromoléculaires n'est pas la même dans toutes les structures: elle est perpendiculaire au plan des feuillets, dans la structure en feuillets; radiale dans la structure en cylindres ou en sphères. De même, la configuration des chaînes n'est pas la même dans les différentes structures observées. Ceci ressort clairement de la différence des valeurs des surfaces spécifiques que mesurent l'encombrement des chaînes au niveau des interfaces.

Il est intéressant de souligner l'importance de la teneur en solvant sur la configuration des macromolécules. Dans le cas du Tétronic 904 en

présence d'eau, par exemple, nous avons observé selon la concentration, quatre structures, donc quatre configurations, différentes: une structure en feuillets avec les séquences POE "cristallisées" pour le copolymère "sec," puis dans l'ordre des teneurs en eau croissantes, une structure en feuillets avec les séquences POE désordonnées, une structure en sphères et finalement une structure en cylindres.

Enfin, nous avons montré qu'en absence d'un solvant des séquences POE, celles-ci adoptent, dans les phases mésomorphes, une configuration "cristalline." Cette configuration n'est cependant pas unique. Lorsque la longueur des séquences POE dépasse une certaine valeur, celles-ci, tout en restant "cristallisées," se replient sur elles-mêmes; de même, lorsque le solvant utilisé n'est pas un précipitant du POE (le nitrobenzène, par exemple), la configuration des séquences POE "cristallisées" dépend de la teneur en solvant, puisque les chaînes s'inclinent progressivement par rapport au plan des feuillets.

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Résumé

Les copolymères séquencés polystyrolène–polyoxyéthylène et polyoxypropylène–polyoxyéthylène, mis en présence d'un solvant préférentiel soit du polystyrolène ou du polyoxypropylène, soit du polyoxyéthylène, fournissent à concentration élevée des gels spontanément biréfringents, présentant les textures anisotropes des phases mésomorphes. L'examen au moyen de la diffraction des rayons X de ces gels permet de déceler une organisation bien développée à l'échelle des 100–500 A; celle-ci, dans la majeure partie des cas, est du type lamellaire, ou alors du type en cylindres ou en sphères. La configuration des macromolécules est telle que les différentes séquences se localisent dans des régions distinctes et juxtoposées dans l'échantillon, tout en y préservant leur individualité. En étudiant ces structures nous avons pu dégager certaines conclusions sur la configuration des chaînes macromoléculaires et sur les paramètres qui la déterminent.

Synopsis

When polystyrene–poly(ethylene oxide) and poly(propylene oxide)–poly(ethylene oxide) block copolymers are mixed with preferential solvents of polystyrene, poly(pro-

pylene oxide), or poly(ethylene oxide), they give, at high concentrations, birefringent gels which exhibit the anisotropic textures of mesomorphic phases. The study of these gels by means of x-ray diffraction techniques shows a well developed organization in the range of 100–500 A.; this organization is of the lamellar, cylindrical, or spherical type. The configuration of the macromolecules corresponds to the localization of the blocks within distinct and neighboring regions in the sample, where they conserve their individuality. In studying these structures we have been able to arrive at certain conclusions as to the parameters which determine the configuration of macromolecular chains.

Zusammenfassung

Aus Blockcopolymeren kann man, in Gegenwart eines bevorzugten Lösungsmittels des einen Blocks, spontan doppelbrechende Gele erzeugen, die die Anordnung und charakteristische Eigenschaften der mesomorphen Phasen aufweisen. Diese Arbeit bringt Ergebnisse hervor, die an Polystyrol–polyäthylenoxyd und an Polypropylenoxyd–polyäthylenoxyd Blockcopolymeren erhalten wurden. Röntgenstrahlendiffraktionsspektren erlauben, im Gebiet von 100 bis 500 A eine gut entwickelte Organisation machzuweisen. In den meisten Fällen ist diese von schichtenförmigem aber manchmal auch von zylindrischem oder spherischem Typ. Die einzelnen Sequenzen ordnen sich in verschiedartigen aber benachbarten Raumgebieten, so dass sie ihre Eigenarten behalten. Das Studium dieser Strukturen hat es uns erlaubt, einige Schlussfolgerungen zu zielen über die Gestaltung der Makromoleküle und über die Parameter, die sie regieren.

Discussion

W. Prins (*Laboratory for Physical Chemistry, Delft, Hollande*): Quels sont les facteurs qui déterminent le système que l'on obtient: en feuillets, en cylindres, etc.?

A. E. Skoulios: Les systèmes que nous avons examinés sont trop peu nombreux pour que l'on puisse préciser clairement les facteurs qui déterminent le type de structure obtenue. Outre le facteur "teneur du système en solvant" qui est traité dans notre exposé, il semble que dans le cas où le copolymère considéré contient des séquences cristallisables, et que l'on opère en présence d'un précipitant de celles-ci, la structure obtenue est lamellaire. Dans le cas contraire, et par analogie avec ce que l'on sait des amphiphiles micromoléculaires non ioniques [cf., Luzzati, Mustacchi, Skoulios, et Husson, *Acta Cryst.*, **13,** 660 (1960)], [Husson, Mustacchi, et Luzzati, *Acta Cryst.*, **13,** 668 (1960)]; on peut s'attendre à des structures en feuillets lorsque l'encombrement des séquences solubles est relativement faibles, à des structures en sphères lorsque celui-ci est important, et à des structures en cylindres lorsque cet encombrement est intermédiaire.

J. Corbiere (*Rhodiacéta, Lyon, France*): D'après la structure des differentes formes que vous avez présentées, on peut penser qu'au délà d'une certaine dilution on devrait aboutir: (*a*) à un gel (uniquement) avec les combinaisons donnant des structures à feuillets; (*b*) à une solution (± gelifiée) avec les combinaisons donnant des structures à cylindres; (*c*) à une veritable solution (± coloidale) avec les combinaisons donnant des structures "sphères."

A. E. Skoulios: Les structures que nous venons de décrire sont celles de systèmes à l'équilibre thermodynamique; leur domaine de stabilité est donc bien défini. A des dilutions grandes, on est en présence d'une solution micellaire non organisée. Il n'est pas exclu que la forme des micelles sont en relation avec celle des éléments de structure des phases mésomorphes concentrées; il convient néanmoins de rappeler le cas du système tétronic 904—eau examiné plus haut, où l'on remarque l'importance que peut avoir la teneur en solvant sur le type de structure adopté par le système.

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Analysis of Copolymers by Means of Density Gradient Centrifugation

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Introduction

It has been shown in theoretical work[1,2] that the density gradient centrifugation of a mixture of polymers can give quantitative information regarding the distribution over molecular weight and chemical composition. This will be particularly useful in the study of copolymers, block copolymers, and grafts. The theory of the method is based on the pioneering work of Meselson, Stahl, and Vinograd,[3] who showed that the equilibrium distribution of a homogeneous polymer over the centrifuge cell in a density gradient is represented to a good approximation by a Gaussian curve, the width of which is inversely proportional to the square root of the molecular weight. The maximum of this Gaussian is situated at the position where the density of the mixture that is used to establish the gradient is equal to the effective density of the polymer, but this effective density is, as a rule, not equal to the reciprocal of the partial specific volume of the polymer because it may be affected by preferential absorption of one of the solvents.[4–7]

If now the method is applied to a mixture of polymers, the total distribution becomes the superposition of numerous Gaussian curves, many of which have their maximum at a different position depending on the effective density of the polymer species that is collected in this Gaussian band. The quantity that is measured in practice is the contribution of the polymer to the absorption of light or to the refractive index (or, if schlieren optics are used, the gradient of the refractive index).

It is assumed that the contribution of a polymer species with effective density ρ_e to refractive index or to light absorption is proportional to the volume fraction Φ of this species and may be written $s(M,\rho_e)\Phi$, where s is a function of the molecular weight M and the effective density ρ_e. In most cases the function s is independent or nearly independent of M, but this is immaterial for the present argument.

Let r represent the distance from the center of rotation. The light absorption or refractive index will be represented by $F(x)$, a function of the distance

$$x = r - \tilde{r} \tag{1}$$

from some arbitrary position $\bar{r}$ in the polymer band. On the assumption that the density of the liquid mixture over the entire band is a linear function of x, one has[1,2,8]

$$F(x) = (\lambda/\pi)^{1/2} \int_0^\infty dM \int_{-\infty}^{\infty} d\epsilon h(M,\epsilon) M^{1/2} \exp\left\{-\lambda M(x - \epsilon/b)^2\right\} \quad (2)$$

Here ϵ represents the difference between ρ_e and the effective density of the species which collects around $\bar{r}$. The distribution over molecular weight M and effective density ρ_e in the sample is given by the weight distribution $f(M,\epsilon)$ and

$$h(M,\epsilon) = s(M,\epsilon) f(M,\epsilon) \quad (3)$$

Furthermore, b is the value of the density gradient in the band

$$\lambda = (\omega^2 \bar{r}/2RT) b/\rho_e \quad (4)$$

where ω is the angular velocity. It is to be noted that the derivation of eq. (2) is based on the assumption that polymer interaction is negligible. This requires that the experiments are done close to theta conditions and that the results are extrapolated to zero polymer concentration.

It is convenient to introduce the auxiliary quantities

$$P = \lambda M \quad (5)$$

$$w = \epsilon/b$$

and to write, accordingly,

$$F(x) = \pi^{-1/2} \int_0^\infty dP \int_{-\infty}^{\infty} dw P^{1/2} h(P,w) \exp\left\{-P(x - w)^2\right\} \quad (6)$$

The function F may then be used[2,8] to obtain averages of the type $\langle P^k \rangle$, $\langle P^k w \rangle$, and $\langle P^k w^2 \rangle$, where the average of a function $\varphi(P,w)$ is defined as follows:

$$\langle \varphi \rangle \int_0^\infty dP \int_{-\infty}^{\infty} dw h(P,w) = \int_0^\infty dP \int_{-\infty}^{\infty} dw \varphi(P,w) h(P,w) \quad (7)$$

The averages considered may be reduced further by writing

$$P = P_0(1 + m) \quad (8)$$

where $P_0 = \langle P \rangle$, so that $\langle m \rangle = 0$. The value of P_0 is close to the weight average.[2] If the distribution over P is sufficiently narrow to restrict all considerations to the moments $\langle m^2 \rangle$, $\langle w \rangle$, $\langle mw \rangle$, and $\langle w^2 \rangle$, it is obvious that

$$\langle P^k \rangle = P_0^{\,k} + {}^1/_2 k(k - 1) P_0^{\,k} \langle m^2 \rangle \quad (9)$$

$$\langle P^k w \rangle = P_0^{\,k} \langle w \rangle + k P_0^{\,k} \langle mw \rangle \quad (10)$$

$$\langle P^k w^2 \rangle = P_0^{\,k} \langle w^2 \rangle \quad (11)$$

Under these circumstances it is possible[2] to express integrals over $x^n F(x)$ for a variety of n values in terms of the five parameters P_0, $\langle w \rangle$, $\langle mw \rangle$, $\langle m^2 \rangle$,

and $\langle w^2 \rangle$. In the present work, use was made of schlieren optics, which means that the quantity measured was the function

$$g(x) = -dF/dx \tag{12}$$

Integrals over $x^nF(x)$ may, however, be reduced to integrals over $x^{n+1}g(x)$ by partial integration. The following abbreviations are used:

$$S_n{}^+ = \int_0^\infty dx x^n g(x) \tag{13}$$

$$S_n{}^- = \int_{-\infty}^0 dx(-x)^n g(x) \tag{14}$$

The point $x = 0$ (i.e., $r = \tilde{r}$) is chosen at the position where $g(x) = 0$. As shown in previous work,[2] this leads at once to the equation

$$\langle P^{1/2} w \rangle = 0 \tag{15}$$

which becomes

$$2\langle w \rangle + 3\langle mw \rangle = 0 \tag{16}$$

when eq. (8) is used for small values of m and w. It further follows from eq. (2) by straightforward manipulations, assuming that integrations may be exchanged in order, that

$$\pi^{1/2} S_n{}^+ = \Gamma\left(\frac{n}{2} + 1\right)\langle P^{-\frac{n}{2}+\frac{1}{2}} \rangle + n\Gamma\left(\frac{n}{2} + \frac{1}{2}\right)\langle P^{-\frac{n}{2}+1} w \rangle + (n-1)\Gamma\left(\frac{n}{2} + 1\right)\langle P^{-\frac{n}{2}+\frac{3}{2}} w^2 \rangle. \tag{17}$$

The expression for $S_n{}^-$ is found by inserting $-w$ for $+w$ and changing the sign. In other words $S_n{}^-(P,w) = -S_n{}^+(P,w)$.

To investigate the applicability of these relations to actual copolymers, a study was made with a copolymer of styrene and iodostyrene. It is not possible to establish theta conditions for all polymer species in the sample simultaneously, so that extrapolation to zero polymer concentration is essential. Now, the difference

$$A = S_1{}^+ - S_1{}^- \tag{18}$$

is proportional to the integral over $F(x)$ from $-\infty$ to $+\infty$ and is therefore proportional to the total amount of polymer present. The procedure to be used for extrapolation is, therefore, to plot $S_n{}^+/A$ and $S_n{}^-/A$ versus the initial concentration of the polymer (compare in this connection reference 6).

Sample Used

A copolymer of iodostyrene and styrene was kindly put at the authors' disposal by Dr. Braun, Deutsches Kunstoff Institut, Darmstadt, Germany. The degree of conversion was 64%. From the reactivity constants r_1 and r_2 reported by Walling, Briggs, Wolfstirn, and Mayo[9] it was calculated[10]

that the iodine content in the sample varies from about 20 to about 27 wt.-%, with an average of 24.15 wt.-%.

Dr. Braun likewise supplied us with a sample from which the iodine had been removed.[11] This author has given arguments to show that in this procedure there is no change in degree of polymerization.[12] The intrinsic viscosity of the polymer from which the iodine had been removed, in toluene at 20°C, was found to be 72 ml./g. According to Meyerhoff,[13] this means that the weight-average molecular weight is close to 176,000. The iodated sample has, therefore, a molecular weight of 230,000.

From density gradient centrifugation of the iodine-free polymer it was concluded that M_w/M_n is in the neighborhood of 2. The procedure for obtaining this result has been described previously.[6] It will be tentatively assumed, on the basis of this result, that the molecular weight distribution is not far from the so-called "most probable" one, in which the weight of polymer with molecular weight M is proportional to $M \exp\{-2M/M_w\}$.

Equilibrium in the Ultracentrifuge

After extensive studies of several solvent mixtures, a system was found which has the appropriate density and is very nearly a theta solvent for the copolymer with 24% iodine. This system is 1-chloropentane at 12° C., which contains 0.814 g. tetraethyllead/ml. mixture. The following four initial concentrations of polymer were examined: 1.11, 2.40, 3.79, and 6.12 g./l.

Since it was found that some of the polymer precipitated when the temperature decreased below 12°C., centrifugation for the first 12 hr. was carried out at 25°C. to make sure that no precipitation occurred during approach to equilibrium. The measurements were carried out in a Spinco double-sector cell, filled Epon, modified according to Ende.[8,14] The refer-

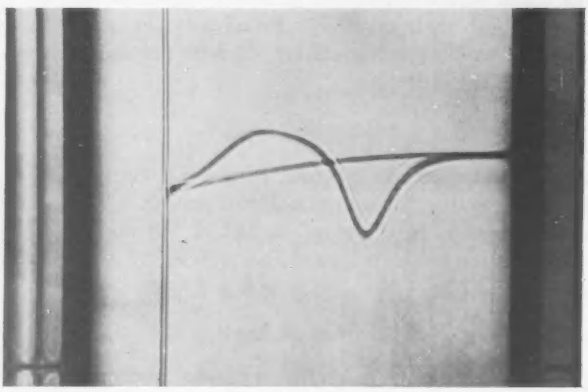

Fig. 1. Schlieren diagram, i.e., $-g(x)$ vs. x, for the sample investigated when the initial polymer concentration in the cell is 3.79 g./l. The base line originates from the polymer-free solvent mixture in the reference sector.

ence sector was filled with the polymer-free solvent mixture, so that in the schlieren photograph both the polymer band and the base line appear. Figure 1 shows the result obtained for an initial polymer concentration of 3.79 g./l. at an angular speed of 42,040 rpm. The curve is clearly unsymmetrical, which is evidence for a composition distribution.[1,3] The curves obtained at the other polymer concentrations are very similar.

By using the procedure explained by Hermans and Ende,[6] the density and the density gradient at the position $\tilde{r}$ were estimated, with the results

$$\tilde{\rho}_e = 1.257 \text{ g./cm.}^3$$

$$b = 0.158 \text{ g./cm.}^4$$

This led to a value of 3.39×10^{-4} for λ. Multiplying this by the value 230,000 for M, it is found that the parameter P_0 defined in eq. (8) has the value 78 cm.$^{-2}$

Evaluation of the Curves

For each of the curves, the integrals S_n^+ and S_n^- were determined for $n = 3, 2.5, 2, 1.5, 1, 0.5, 0$, and -0.5. The difference between S_1^+ and S_1^- determines A. Plots of S_n^+/A and S_n^-/A versus initial polymer concentration c are good straight lines up to c about 4.5 g./l. A few examples are shown in Figure 2.

Attempts were made to determine, in addition, the values of S_{-1}^+/A S_{-1}^-/A, and $A^{-1}(dg/dx)_{x=0}$, but plots of these quantities versus c showed, too much scatter and too steep a slope for a reliable extrapolation, and the use of these quantities had to be abandoned.

The eqs. (17) were written in terms of the parameters P_0, $\langle w \rangle$, $\langle mw \rangle$, $\langle m^2 \rangle$, and $\langle w^2 \rangle$ through the use of the approximation made in eqs. (9), (10), and (11). This approximation is valid only when $\langle m^2 \rangle$ is small compared with unity, and this is not true in the present investigation. In fact, if the distribution over P is approximately given by the expression $P \exp\{-2P/P_0\}$, as assumed, one must expect that $\langle m^2 \rangle = 0.5$. There may be an additional fluctuation in P as a result of the compositional distribution, so that $\langle m^2 \rangle$ in the sample investigated may well be as high as 0.6 or 0.7. It will be shown, however, that the experimental results are not very sensitive to changes in the value chosen for $\langle m^2 \rangle$, and it is therefore believed that little would be gained by a more rigorous treatment of the data.

The equations obtained are linear in the four parameters $\langle w \rangle$, $\langle mw \rangle$, $\langle m^2 \rangle$, and $\langle w^2 \rangle$, but not in P_0. It was found that P_0 could be varied within wide limits (at the same time adjusting the values of the other parameters) without seriously affecting the agreement between the calculated and observed values of S_n^+/A and S_n^-/A. This means that the experimental results do not suffice to use them for a straightforward computation of all five parameters. It was therefore decided to insert the value $P_0 = 78$ (see the end of the previous section). The final equations thus become linear in $\langle m \rangle$, $\langle mw \rangle$, $\langle m^2 \rangle$, and $\langle w^2 \rangle$. Each of these equations, however, is

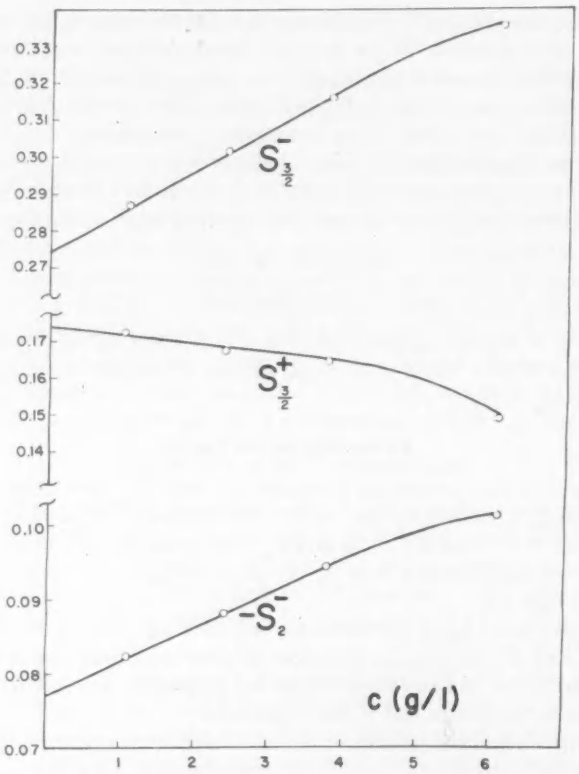

Fig. 2. Examples of the extrapolation of S^+_n/A and S^-_n/A for some values of n to zero polymer concentration c.

affected by the possible experimental errors in S_n^+/A and S_n^-/A, to an extent that depends, moreover, on the value of n. The solution of these equations should therefore be obtained statistically, giving appropriate weight to each equation individually. The procedure adopted, however, was a simple method of trial-and-error, which led to the following values:

$$\langle w \rangle = -0.032 \text{ cm.}$$

$$\langle mw \rangle = 0.022 \text{ cm.}$$

$$\langle m^2 \rangle = 0.80$$

$$\langle w^2 \rangle = 0.0046 \text{ cm.}^2$$

When these values are used to calculate S_n^+ and S_n^-, Table I is obtained, which shows good agreement between calculated and experimental values. However, equally good agreement is observed when assuming the same

values for $\langle w \rangle$ and $\langle mw \rangle$ but inserting $\langle m^2 \rangle = 0.70$ and $\langle w^2 \rangle = 0.0049$. The permissible variation in $\langle m^2 \rangle$ would become even larger if one considered slightly different values of $\langle w \rangle$ as well. A reliable estimate of the uncertainty in the fluctuations would require a complete statistical analysis. As regards order of magnitude, it is possible to say on the basis of trial-and-error, that the uncertainty is of the order of 25% in $\langle m^2 \rangle$ and 10–15% in $\langle w^2 \rangle$.

TABLE I

Comparison of the Experimental Values of S_n^+/A and S_n^-/A with those calculated on the assumption that $\langle w \rangle = -0.032$ cm., $\langle mw \rangle = 0.022$ cm., $\langle m^2 \rangle = 0.80$, $\langle w^2 \rangle = 0.0046$ cm.^{2}, using the value 78 cm.$^{-2}$ for P_0

	S^+/A, cm.$^{n-1}$		S^-/A, cm.$^{n-1}$	
n	Calcd.	Exptl.	Calcd.	Exptl.
3	0.016	0.017	0.033	0.036
2.5	0.034	0.033	0.067	0.071
2.0	0.076	0.081	0.140	0.146
1.5	0.168	0.173	0.288	0.274
1.0	0.41	0.42	0.59	0.58
0.5	0.99	1.04	1.27	1.22
0.0	2.4	2.7	2.4	2.7
−0.5	8.1	7.9	6.0	6.6

Finally, it is clear that the real fluctuation in w is determined by the magnitude of $\Delta^2 = \langle w^2 \rangle - \langle w \rangle^2$. Assuming the values given, this means that Δ^2 is about 0.0035 cm.^{2}

Conclusion

The data and their evaluation show that valuable information can indeed be derived from the centrifugation equilibrium in a density gradient. It is necessary, however to use some additional information from independent sources. In the present study this was done on the basis of the average molecular weight to determine the parameter P_0. In other cases it may be done on the basis of some independent information concerning $\langle w^2 \rangle$ or $\langle w \rangle$ that could then be used to obtain the values of the other parameters with greater accuracy.

The technical assistance of G. D. Howard and J. O. Threlkeld is gratefully acknowledged.

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Synopsis

According to a previously developed theory, the equilibrium distribution of a copolymer in density gradient centrifugation can give quantitative information concerning the average molecular weight, and the fluctuations in molecular weight and composition. To investigate the applicability of this new method, a study is made of a copolymer of styrene and iodostyrene, the iodine content of which fluctuates between about 20 and 27 wt.-%. It is found that the experimental results can be used to estimate the fluctuations in molecular weight and effective density, provided the average molecular weight is known. Even under these circumstances, the possible error of the fluctuations calculated from the data is of the order of 20%.

Résumé

En accord avec une théorie déjà développée, la distribution à l'équilibre d'un copolymère obtenu par centrifugation suivant le gradient de densité, peut fournir des renseignements quantitatifs au sujet du poids moléculaire moyen, et des variations dans le poids moléculaire et la composition. Afin de déterminer l'applicabilité de cette nouvelle méthode, on a étudié un copolymère de styrène et d'iodostyrène, dont la teneur en iode varie de 20 à 27% en poids. On a constaté que les résultats expérimentaux peuvent être utilisés en vue d'estimer les variations du poids moléculaire et de la densité effective, pourvue que le poids moléculaire moyen soit connu. Même dans ces conditions, l'erreur possible des variations calculées à partir de ces résultats est de l'ordre de 20%.

Zusammenfassung

Nach einer früher entwickelten Theorie kann die Gleichgewichtsverteilung eines Copolymeren bei der Zentrifugierung mit Dichtegradienten quantitative Aufschlüsse über das mittlere Molekulargewicht und die Molekulargewichts- und Zusammensetzungsschwankungen liefern. Um die Verwendbarkeit dieser neuen Methode zu überprüfen, wurde die Untersuchung eines Styrol-Jodstyrol-Copolymeren mit einer Schwankung des Jodgehaltes zwischen etwa 20 und 27 Gew. % durchgeführt. Bei Kenntnis des mittleren Molekulargewichts können die Versuchsergebnisse zur Bestimmung de Schwankungen des Molekulargewichts und der effektiven Dichte herangezogen werden. Selbst unter dieser Voraussetzung beträgt der mögliche Fehler der aus den Daten berechneten Schwankungen grossenordnungsmässig 20%.

Discussion

H. Eisenberg (*Weizmann Institute of Science, Rehovot, Israel*): Measurements were done close to the theta point at various concentrations of polymer, and the results were extrapolated to zero polymer concentration to eliminate non-ideality effects. Fluctuations in the molecular weight are accounted for by the mathematical analysis itself.

In fact, this analysis allows one in principle to draw conclusions with regard to both fluctuations in molecular weight and fluctuations in composition.

W. Prins (*Laboratory for Physical Chemistry, Delft, Hollande*): Would the U. C. density gradient method be sensitive enough to determine whether the first approximation method for calculating the fluctuation in composition is indeed insufficient and has to be replaced by a higher approximation method for calculating the fluctuation? (As has been proposed in the literature.)

J. J. Hermans: It is difficult to say at this early stage of the investigations whether the method will ever be sufficiently accurate to decide if the reactivity ratios are constant. At this stage, in any case, the results are *definitely not* sufficiently accurate to decide a question of this nature. Personally I believe that they will be, but it is conceivable that new developments in the technique will at some later time change this situation.

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Graft and Block Copolymers of Some Vinyl Aromatic Hydrocarbons*

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I. INTRODUCTION

The aromatic moieties of vinyl polymers such as polyvinylbiphenyl and polyvinylnaphthalene react in solution with alkali metals to form colored charge transfer complexes referred to as polyradicalanions.[1] These initiate the polymerization of ethylene oxide by bond formation thus leading to graft polymers. Experimental evidence for bond formation was obtained with the biphenyl and naphthalene molecules. The position of attack of substituted aromatic rings by ethylene oxide could be correlated with calculated π-electron densities. The calculations were carried out using the HMO approximation and allowing for the induction effect of substituents. In order to establish optimum conditions for graft formation a study was made of the stability of several polyradicalanion species. The polyradicalanions undergo chain scission at ambient temperature by a mechanism which involves electron localization on the aliphatic α-carbon atom and, ultimately, formation of carbanionic chain ends. The relative stabilities of the aromatic systems considered are related to the π-energy changes involved in the bond scission reaction.

Graft and block copolymers having a backbone of poly-4-vinylbiphenyl (PVB) or poly-2-vinylnaphthalene (PVN) and branches of polyethylene oxide (PEO), were prepared. These polymers were characterized by their solubility behavior as well as by chemical and spectral analyses. Torsional modulus versus temperature determinations provided information about the mechanical properties and glass transition temperatures of these materials. Comparisons were made with the behavior of the homopolymers and their blends.

II. EXPERIMENTAL

1. Purification of Materials

4-Vinylbiphenyl and 2-vinylnaphthalene were purified by passing each monomer in benzene and *n*-hexane solution (50 wt.-%) through a column

* This paper presents one phase of research performed by the Jet Propulsion Laboratory, California Institute of Technology, sponsored by the National Aeronautics and Space Administration, Contract NAS7-100.

of activated alumina. After rejecting the first fraction (10% of the monomer by weight), eluting with pure benzene, and evaporating the solvent, the monomers were crystallized from methanol and dried. 4-Vinylbiphenyl melted at 117°C. and 2-vinylnaphthalene at 65°C.

Ethylene oxide was distilled from solid caustic potash into glass ampules through a column filled with glass beads covered with a thin film of sodium.

Tetrahydrofuran (THF) was purified by reacting it with a sodium potassium alloy and then distilling from a sodium mirror.

2. Anionic Polymerization of 4-Vinylbiphenyl

4-Vinylbiphenyl reacted with sodium in THF was used as initiator. The polymerization technique in high vacuum was previously described.[2] Using decreasing amounts of initiator, molecular weights of 70,000 to 500,000 were obtained. The weight-average molecular weights ($\bar{M}_w$) were estimated from a previously determined relationship.[3]

3. Emulsion Polymerization

Larger quantities of both PVB and PVN were prepared by emulsion polymerization in the following way. 2-Vinylnaphthalene (20 g.), distilled water (500 ml.), potassium persulfate (0.01 g.), and Triton X-100 (0.5 g.) were stirred in a nitrogen atmosphere at 95°C. for 7 hr. The formed polymer was filtered, dried, redissolved in benzene, precipitated with methanol, filtered, and dried at 60°C. in a vacuum oven for 14 hr.; yield 12.7 g.

The intrinsic viscosity in benzene was 1.17; the estimated[4] molecular weight was 950,000. 4-Vinylbiphenyl polymerized in an identical way yielded a polymer with $[\eta] = 0.73$ ($\bar{M}_w = 460{,}000$).

4. Graft Formation

All operations were carried out in dry glass apparatus and all reagents thoroughly degassed under a pressure of 10^{-5} mm. Hg. The technique for transfer of reagents and preparation of metallic cesium was already described.[2] PVB or PVN dissolved in THF reacted with a cesium mirror at −80°C. to give blue and green solutions, respectively. After addition of ethylene oxide the temperature was raised to 0°C. The mixture became viscous within 30 min. to 4 hr. and was kept for 24 hr. at room temperature to assure complete reaction. The anionic chain ends were deactivated by 0.5 ml. of methanol or methyl iodide; *n*-hexane was then added, and the polymer filtered and dried in vacuum. 100% yields were obtained in all experiments.

5. Block Formation

A PVB–EO block polymer was prepared by a method similar to the one used for the preparation of polystyrene–ethylene oxide blocks.[5] 4-Vinylbiphenyl was polymerized using cesium initiation as described previously,[2]

and ethylene oxide was added at 0°C. The subsequent steps were identical to the procedure described above for graft formation.

6. Characterization of Products

a. Analyses. The weight per cent PVB in a water-extracted graft polymer was determined by using the extinction coefficient of PVB at 254 mμ found to be equal to 110 l./g.-cm. in dimethoxyethane. The PEO content was determined from the extinction coefficient of pure PEO at 9 μ in chloroform. A calibration curve (Fig. 1) was established by means of PEO–PVB blends of known concentration. Similarly the analysis of PVN was based on the extinction coefficient of pure PVN at 278 mμ found to be equal to 29.3. Visible spectra were recorded on a Beckman DK2, and the ultraviolet and infrared analyses were carried out by means of a Beckman D.U. and Perkin-Elmer Model 21 spectrophotometer, respectively. Both analytical methods are accurate to ±5%. The cesium con-

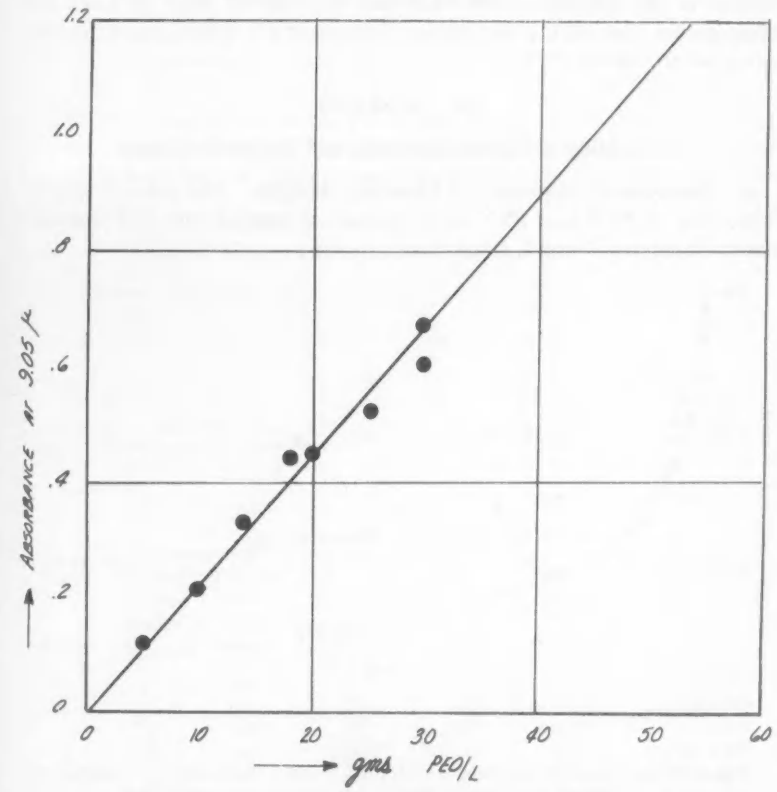


Fig. 1. Absorbance of PVB–PEO synthetic mixtures in chloroform.

centration was determined either by direct titration with 0.1*N* HCl with phenolphthalein as indicator or by titration of NaI, after termination of the active chain ends with methyl iodide. The latter method yielded alkali concentrations 10 to 20% lower than the direct titration procedure.

b. Viscosity. Viscosities of isolated polymer were determined in an Ubbelohde viscometer in benzene at 25 ± 0.5°C. Flow times of polyradicalanions in THF and of solvent were determined in a Cannon Zhukov viscometer, which was modified to enable the determination of viscosities in the absence of air.

c. Young's Modulus. Estimations of Young's modulus were made on a torsional apparatus constructed according to A.S.T.M. standards.[6]

d. ESR Spectra. Electron spin resonance spectra were obtained by means of the 4500 Varian Associates spectrometer on samples dissolved in THF and placed in evacuated quartz or Pyrex glass tubes (4 m. O.D.).

e. Film Molding. The polymer films were prepared by compression of powdered samples between 2,000 and 10,000 psi at temperatures characteristic of the polymer. For PEO and unextracted graft polymer the temperature was 62°C., for pure PVB and PVN 150°C., and for the extracted grafts 105°C.

III. RESULTS

1. Stability of Polyradicalanions and Polymeric Anions

a. Decrease of Viscosity and Molecular Weight. The reduced specific viscosities of PVB and PVN as a function of temperature and time are shown in Figures 2 and 3, respectively.

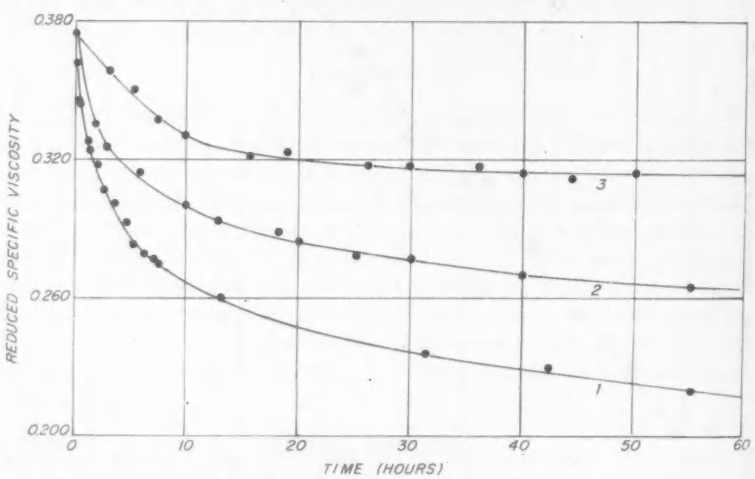


Fig. 2. Reduced specific viscosity of PVB ($\bar{M}_w$ = 184,000) vs. time: (*1*) sodium concentration 3 × $10^{-2}M$, temperature 50°C.; (*2*) sodium concentration 7 × $10^{-3}M$, temperature 50°C.; (*3*) sodium concentration 2.5 × $10^{-3}M$, temperature 25°C.

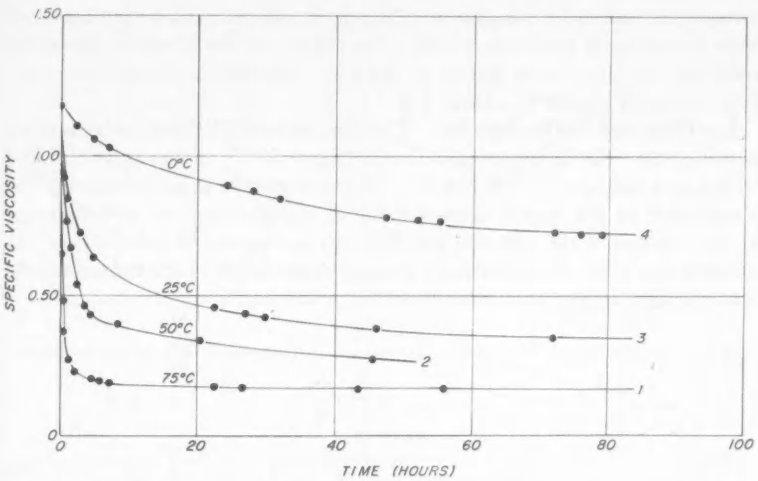


Fig. 3. Specific viscosity of PVN ($\bar{M}_w \simeq 950{,}000$) vs. time at several temperatures at sodium concentration $8 \times 10^{-3}M$: (*1*) 75°C.; (*2*) 50°C.; (*3*) 25°C.; (*4*) 0°C.

Table I shows the actual molecular weight of polymers isolated at various times. Neither PVB nor the PVN complex was degraded when kept at −20°C. for 4 hr. In contrast to polyradicalanions, the long-chain anions

TABLE I
Molecular Weights of PVB Polyradicalanion as a Function of Time

Polymer concentration, g./l.	Sodium concentration, mmoles/l.	Temperature, °C.	Time, hr	Intrinsic viscosity (in benzene)	$\bar{M}_w$
40	4	25	0	0.731	440,000
40	4	25	4	0.568	320,000
40	4	25	232	0.465	250,000

TABLE II
Degradation of PVB Anions with Time

Sample	Sodium concentration, mmoles/l.	Polymer concentration, g./l.	Temperature, °C.	Time, hr.	Intrinsic viscosity (in benzene)	Weight-average molecular weight $\bar{M}_w$
1	7	80	50	0	0.257	100,000
1	7	80	50	24	0.256	100,000
1	7	80	50	200	0.257	100,000
2	3	80	100	0	0.716	455,000
2	3	80	100	24	0.654	390,000
2	3	80	100	264	0.564	330,000

formed by reaction of sodium naphthalene or sodium with 4-vinylbiphenyl were found to be relatively stable. No change in the intrinsic viscosities took place at 50°C. after 200 hr. of heating. Significant degradation, however, occurred at 100°C. (Table II).

b. Color and Visible Spectra. The blue color of PVB polyradicalanions persisted at −80°C. for several days. Above 50°C., however, it changed to red in a matter of a few hours. This corresponds to an increase of the absorbance in the region characteristic of the dianion, i.e., 425–550 mμ, at the expense of the 400–405 and 605–610 mμ bands characteristic of the radicalanion (Fig. 4), indicating a gradual degradation of the radical anions into polymer anions.

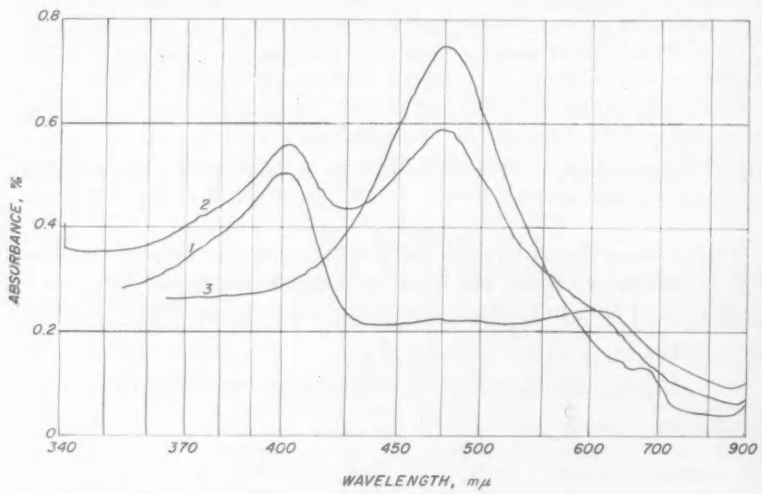


Fig. 4. Spectra of PVB polyradicalanion with time at 50°C.: (*1*) at zero time; (*2*) after 2 hr.; (*3*) after 5 hr.

c. Electron Spin Resonance Spectra. In Figure 5 are shown the spectra of a dilute solution of PVB polyradicalanions when formed and

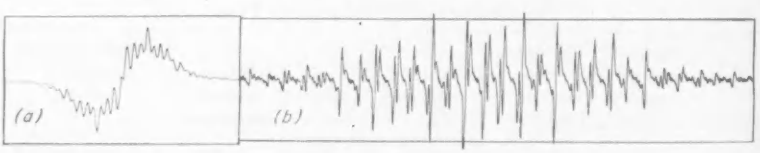


Fig. 5. Electron spin resonance spectrum of PVB on sodium in THF: (*a*) at zero time; (*b*) after 14 days at 0°C.

after two weeks at 0°C. In Figure 6 changes in the ESR signals of PVN polyradicalanions kept at 50°C. are recorded with time. It may be seen

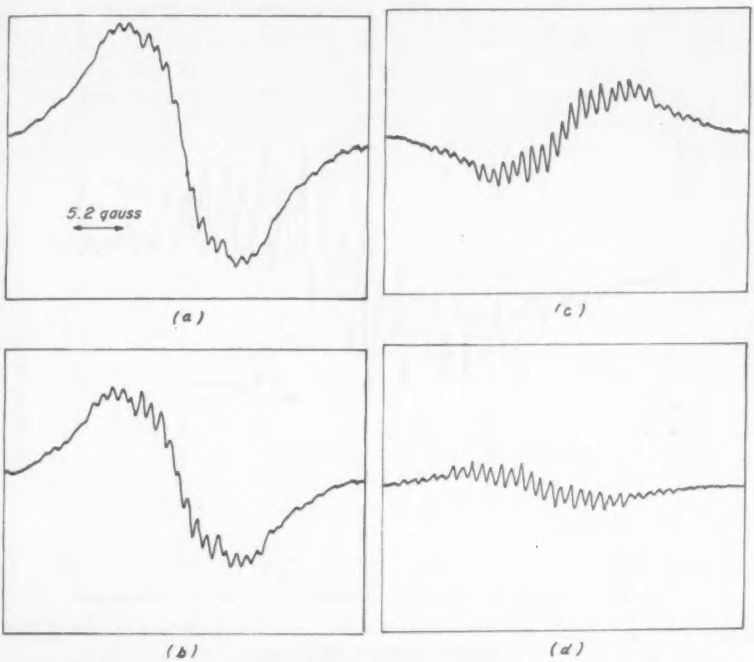


Fig. 6. Electron spin resonance spectrum of PVN on sodium in THF at 50°C.: (*a*) at zero time; (*b*) after 40 min.; (*c*) after 115 min.; (*d*) after 175 min.

from Figure 6c that a concentrated solution of PVN on sodium gives, after a few hours of heating, a spectrum practically identical to that of the original dilute solution (Fig. 7).

2. Bond Formation

a. Reaction with Carbon Dioxide. THF solutions of complexes of PVB with lithium, sodium, and cesium, respectively, were reacted in the

TABLE III
Analysis of PVB after Reaction with CO_2

Alkaline metal	DP[a]	Analyses[b]			CO_2, equiv./chain
		C, %	H, %	O, %	
Na	361	92.98	6.62	0.40	8
Cs	361	93.04	6.77	0.19	4
Na	1000	91.20	6.81	1.99	114
Na	1000	90.74	6.62	2.64	152
Li	361	87.92	6.57	5.51	112

[a] Degree of polymerization estimated from intrinsic viscosities [η] in benzene.

[b] C and H analyses were carried out by Elek Micro-Analytical Laboratories, Los Angeles, California; O was obtained by difference.

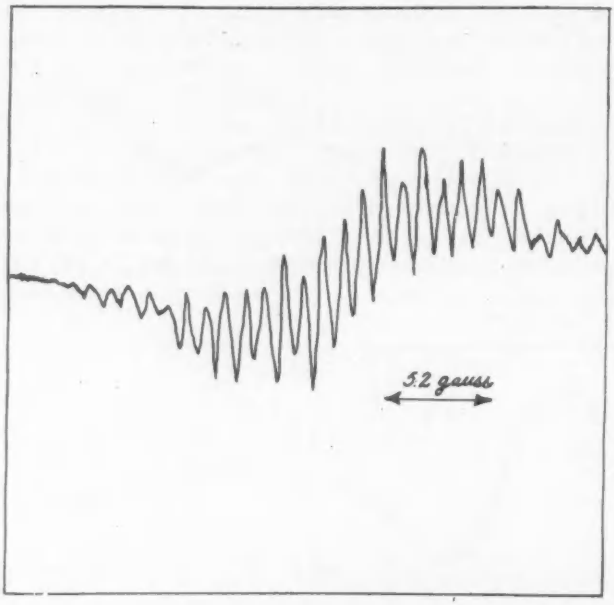


Fig. 7. Electron spin resonance spectrum of a dilute solution of PVN on sodium in THF at zero time before heating.

cold with CO_2. Incorporation of oxygen into the polymer, as evidenced by elemental analysis (Table III), leaves little doubt that the polyradical-anions reacted with CO_2 to produce carboxylic acids. Assuming that each CO_2 reacted with one biphenyl moiety, then between $^1/_{100}$ and $^1/_3$ of the total biphenyls have been converted to radicalanions. Comparison of infrared absorption spectra (Fig. 8) shows that after the CO_2 reaction two absorption bands appeared at 5.85 and 7.8 μ, respectively. The 5.85 μ

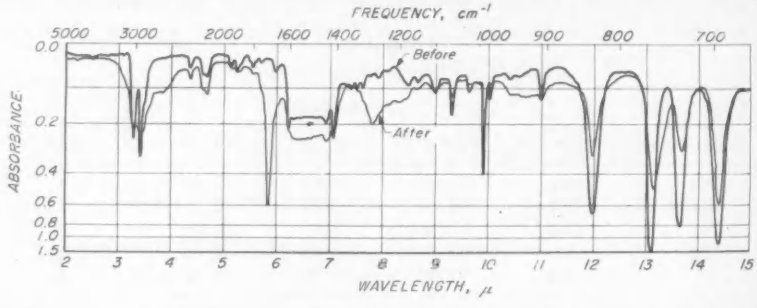


Fig. 8. Absorption spectrum of PVB polyradicalanion before and after reaction with CO_2 in dimethoxyethane (DME).

band is characteristic of CO, and the 7.8 μ band is attributed to the coupled C—O and OH in-plane deformation modes,[7] thus giving further evidence for the carboxylation reaction of polyradicalanions.

b. Reaction with Ethylene Oxide. In order to prove bond formation,

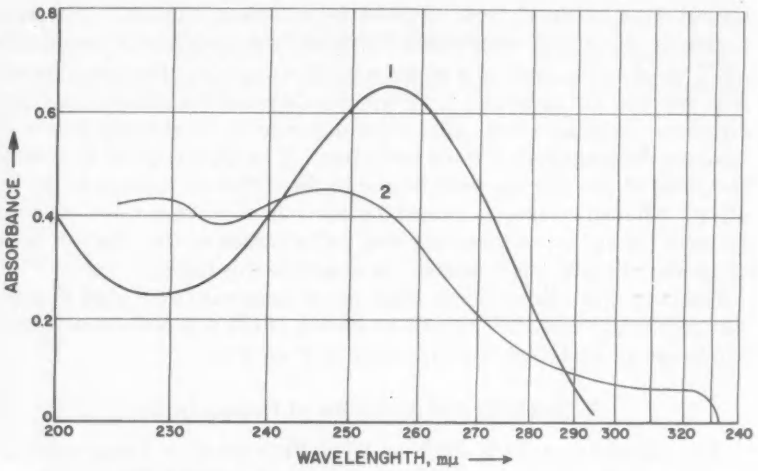


Fig. 9. Absorption spectrum of polyethylene oxide initiated with sodium-biphenyl (*1*) and of biphenyl (*2*) in DME.

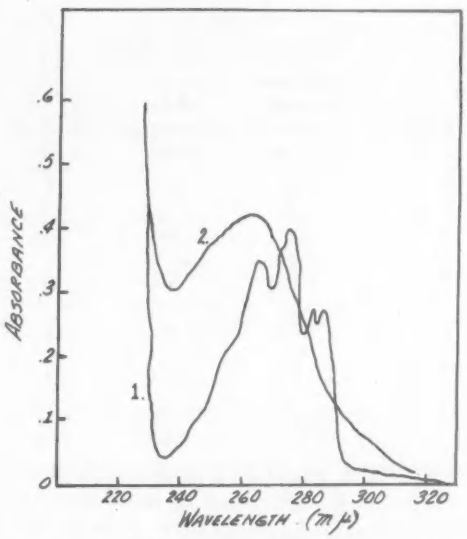


Fig. 10. Absorption spectrum of polyethylene oxide initiated by sodium-naphthalene (*2*) and of naphthalene (*1*) in DME.

the monomeric biphenyl cesium complex (1 g.) was used to initiate the polymerization of ethylene oxide (8 g.) with cesium as the alkali metal gegenion. The reaction proceeded exothermally at 0°C. and was practically completed within minutes. The polymerization rate was considerably decreased when sodium was used instead of cesium, in which case several days at 100°C. were required for complete reaction. The polyoxyethylene initiated with cesium biphenyl was obtained in practically 100% yield in the form of a white amorphous powder after precipitation from acetone with *n*-hexane. This purification method removes any free biphenyl. In Figure 9 the ultraviolet spectrum of the polymer (curve *2*) confirms the hypothesis of bond formation. The appearance of an absorption band at 225–231 mμ must be due to the structural changes of the biphenyl molecule (curve *1*) caused by the formation of a chemical bond between the carbon of a benzene ring and a carbon of the ethylene oxide molecule. Polyoxyethylene does not absorb in this region.

Similarly, when naphthalene alkali metal complexes were used to polymerize ethylene oxide the ultraviolet spectra of the polymer showed structural changes in the naphthalene molecule (Fig. 10).

3. Solubility and Extraction of Homopolymer

The solubility of PVB–PEO or PVN–PEO graft or block polymers varied according to composition. Grafts containing 20–80% of PEO were soluble in benzene, chloroform, tetrahydrofuran, and dimethoxyethane.

TABLE IV
Solubility of Grafts in Water

	Before extraction wt.-%	After water extraction, insoluble phase, wt.-%	wt.-% of insoluble phase	Wt.-% of extract	$\bar{M}_w$
PEO	75	60	53	47	
PVB	25	40			69,000
PEO	50	32	70	30	
PVB	50	68			69,000
PEO	80	67	60	40	
PVB	20	33			450,000
PEO	77	52	48	52	
PVB	23	48			60,000
PEO	77	67	69	31	
PVN	23	33			950,000

Grafts containing 10% or less of PVB were soluble in a 50:50 mixture of methanol and water. All grafts could be dissolved in a mixture of 20% methanol and 80% benzene (by volume).

The PEO homopolymer was separated from grafts containing at least 20% PVB or PVN by means of water extraction. In Table IV are shown

the weights and compositions of the insoluble phase (graft) and soluble phase (mainly PEO) after water extraction. The amount of aromatic polymer in the water extract was of the order of 1%. The molecular weight of the PEO side chains calculated on the basis of alkali metal concentration was found to be of the order of 10,000.

4. Mechanical Properties

The modulus temperature curves for pure PEO (curve *1*) as well as for pure PVN (curve *2*) and PVB (curve *3*) are shown in Figure 11.

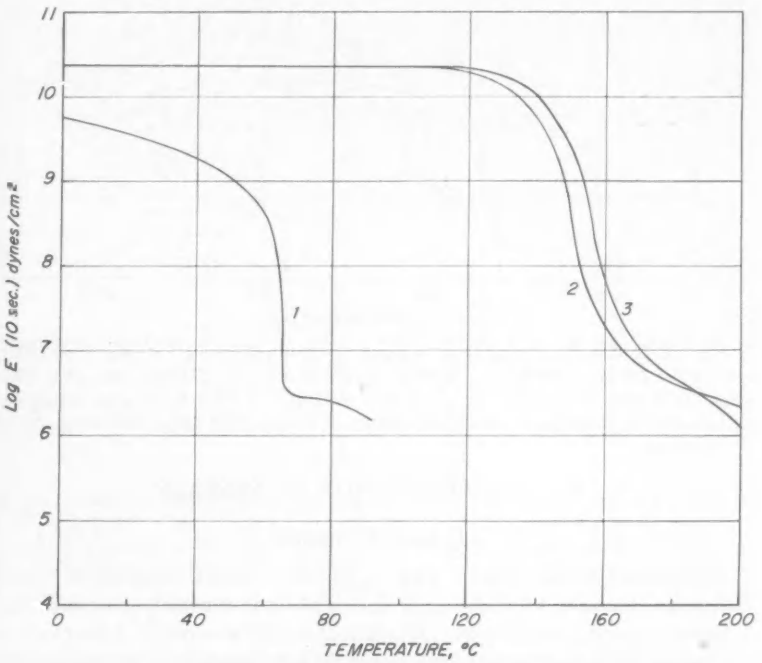


Fig. 11. Torsional modulus versus temperature for homopolymers of: (*1*) PEO ($\bar{M}_w$ = 200,000); (*2*) PVN ($\bar{M}_w \sim$ 950,000); (*3*) PVB ($\bar{M}_w$ = 450,000).

The curves for PVB–PEO grafts are recorded in Figure 12, along with that for a block copolymer of the type PEO–PVB–PEO (curve *4*). The weight-average molecular weight of PEO in the specimens represented by curves *2*, *3*, *4*, and *5* was found to be of the order of 60,000–100,000. The unusual mechanical behavior of PVN–PEO grafts and blends is depicted in Figure 13. The changes in the PVN–PEO graft on heating are reflected in the modulus–temperature curve shown in Figure 14 (curve *2*).

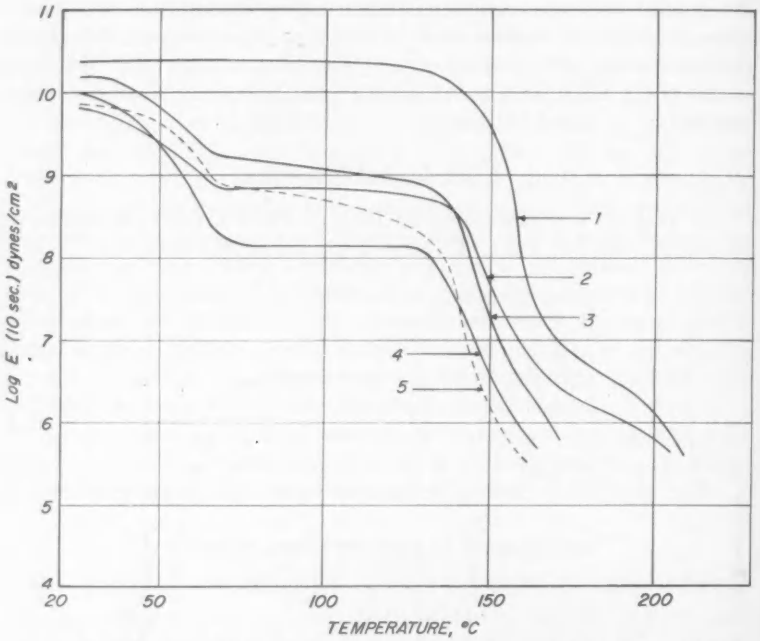


Fig. 12. Torsional modulus versus temperature for: (*1*) Pure PVB ($\bar{M}_w$ = 450,000); (*2*) PVB–PEO graft (PVB 33%, PEO 67%, $\bar{M}_w$ of PVB = 450,000); (*3*) PVB–PEO graft (PVB 80%, PEO 20%, $\bar{M}_w$ of PVB = 69,000); (*4*) PVB–PEO block copolymer (PVB 50%, PEO 50%, M_w of PVB 60,000); (*5*) blend (PVB 50%, PEO 50%, $\bar{M}_w$ of PVB 68,000).

IV. INTERPRETATION OF RESULTS

1. Bond Formation

The spectroscopic results (Figs. 8–10) offer strong evidence for bond formation between ethylene oxide and biphenyl or naphthalene moieties. The isolation of pairs of isomers (I), (II), and (III) as a result of the reaction of sodium naphthalene with stoichiometric amounts of ethylene oxide completes this evidence.[8]

(I)

(II)

(III)

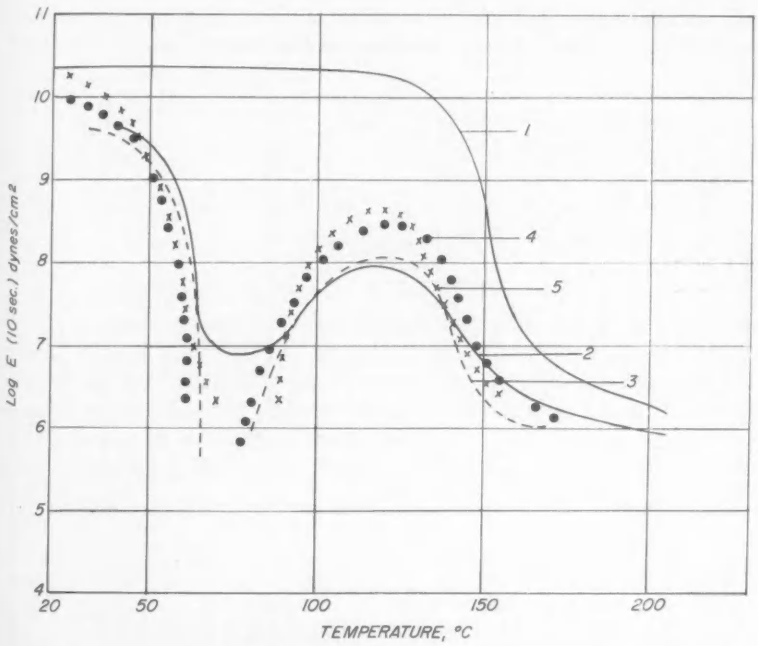


Fig. 13. Torsional modulus versus temperature for: (*1*) pure PVN; (*2*) PVN–PEO graft (PVN 25%, PEO 75%, $\bar{M}_w$ of PVN $\simeq$ 950,000); (*3*) PVN–PEO blend (PVN 25%, PEO 75%, $\bar{M}_w$ of PVN $\simeq$ 950,000); (*4*) PVN–PEO blend (PVN 40%, PEO 60%, $\bar{M}_w$ of PVN $\simeq$ 400,000); (*5*) PVN–PEO blend (PVN 50%, PEO 50%, M_w of PVN $\simeq$ 400,000).

The problem of bond location in a substituted biphenyl or naphthalene molecule remains to be elucidated. The experimental evidence is limited to the reaction of carbon dioxide with 2-methylnaphthalene. It was shown that 2-methylnaphthalene–Na complex reacts with CO_2 to yield 2-methyl-1,4-dihydronaphthalene-1,4-dicarboxylic acid,[9] i.e., bond formation takes place in the substituted ring. The reaction with ethylene oxide is expected to proceed in a similar way. It is likely that both CO_2 and ethylene oxide behave as electrophilic reactants in the transition state. The point of attack would therefore depend on the π-electron densities of a substituted biphenyl or naphthalene. The π-electron densities of 1- and 2-methyl naphthalene as well as 4-methylbiphenyl radical anions were calculated by using the HMO approximation and taking into account the

inductive effect of the methyl group.[10] The results of these calculations are shown in Figure 15.

The highest electron densities are likely to constitute the position of bond formation. The experimental evidence obtained so far is in agreement with these results.[9] Assuming that the aliphatic chain in a PVB or PVN polymer exercises a similar inductive effect to a methyl group, it is possible to predict the position of bond formation with either CO_2 or ethylene oxide

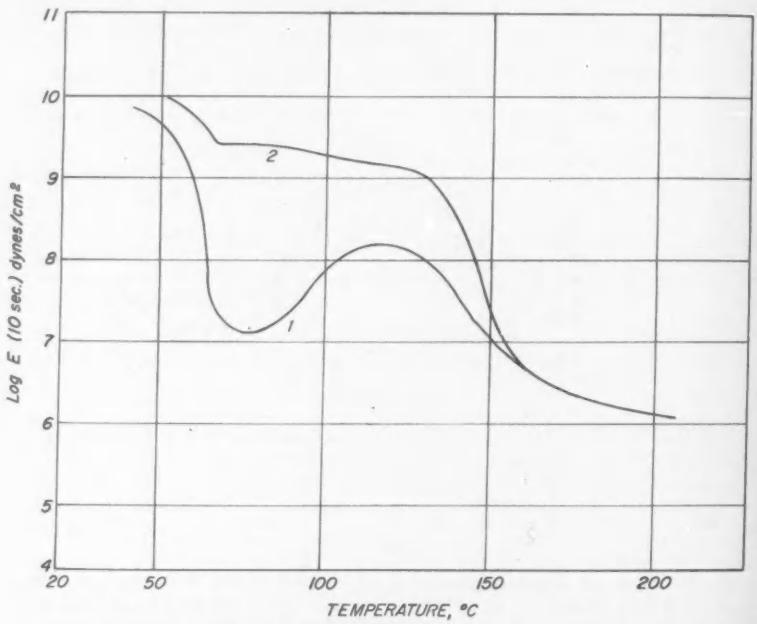
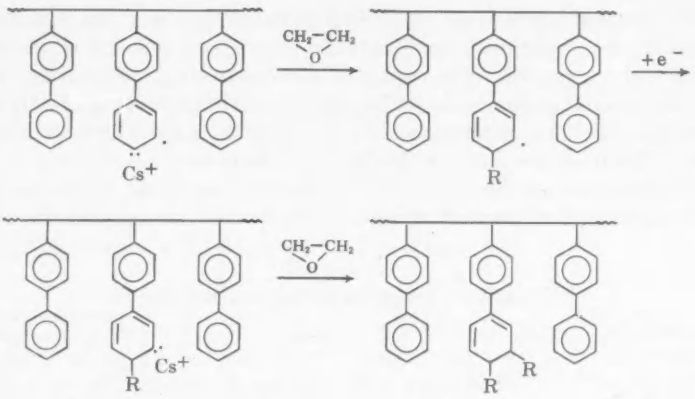


Fig. 14. Torsional modulus versus temperature for PVN–PEO graft (PVN 25%, PEO 75% M_w of PVN $\simeq$ 950,000): (*1*) before heating; (*2*) after heating.

in the cases where direct experimental evidence does not exist. We therefore assume that bond formation in PVB–PEO graft occurs predominantly at the 4′ position of the substituted biphenyl for which the HMO calculations indicate the highest π-electron density. Similarly, addition of ethylene oxide to PVN is expected to take place at position 1 and to 1-methylnaphthalene at position 5, i.e., in the unsubstituted ring.

2. Mechanisms

The mechanism postulated by Paul, Lipkin, and Weissman[11] for the carbonation of the naphthalene radical anion also applies to the formation of PVB or PVN–PEO graft polymers and may be represented by the following sequence of reactions:



where R is $(CH_2–CH_2O)_n$ Cs.

The success of graft formation depends on the stability of polyradicalanions. The latter undergo indubitably a chain scission reaction (Table I), which leads to the formation of anions (Fig. 4). The electron spin resonance study (Figs. 5–7) substantiates the postulate of a loss of free radicals with time. In view of the above results the bond breaking mechanism is probably caused by electron migration from the aromatic rings to the α

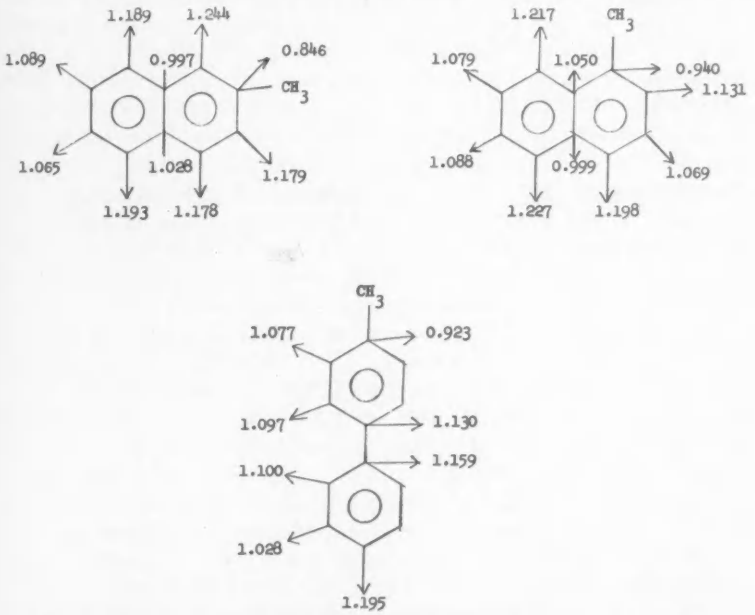


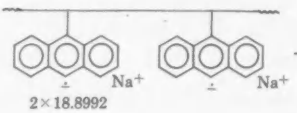
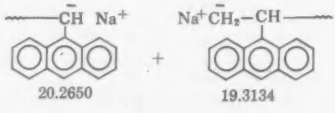
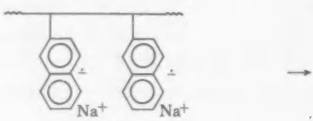
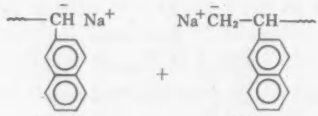
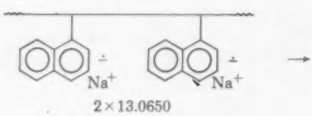
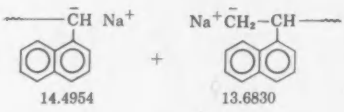
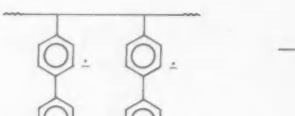
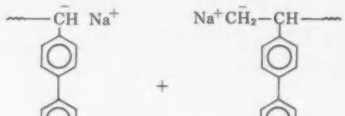
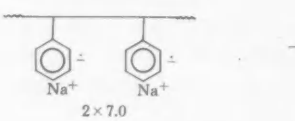
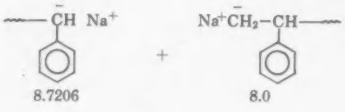
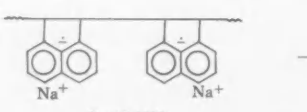
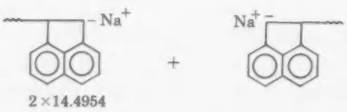
Fig. 15. π-Electron densities of methyl-substituted naphthalenes and biphenyl.

carbon atom of the aliphatic chain.[1] Additional support to the postulated electron migration mechanism is provided by considering resonance energies of the various species. The resonance energies of some radical anions and the corresponding anions, shown in Table V, were calculated by the Huckel molecular orbital approximation. The difference in energies is an indication of the relative stability of the various species.

If we assume that resonance stabilization is the main factor in the formation of anions from polyradicalanions, then Table V implies that the tend-

TABLE V

π-Resonance Energy Gain after Bond Scission

Polyradicalanion	Anions	Energy gain β
 2×18.8992	 20.2650 + 19.3134	1.7800
 2×13.0650	 14.4268 + 13.6830	1.9798
 2×13.0650	 14.4954 + 13.6830	2.0484
 2×15.6786	 17.1395 + 13.6832	2.1655
 2×7.0	 8.7206 + 8.0	2.7206
 2×13.0650	 2×14.4954 +	2.8608

ency of anion formation should increase from poly-9-vinylanthracene which would be expected to be the most stable, to polyacenaphthylene likely to be the least stable. This is in agreement with the experimental results obtained so far. Thus polyacenaphthylene undergoes chain scission instantaneously while PVB and PVN undergo degradation at a measurable rate even at a temperature of 75°C. (Figs. 2 and 3).

It is possible therefore to stabilize the PVB and PVN polyradicalanions at lower temperatures and form grafts with monomers, provided bond formation and not electron transfer is occurring.

3. Solubility and Formation of Homopolymer

Although quantitative polymerization yields could be obtained from all experiments, large amounts of PEO homopolymer were isolated by water extraction in all cases (Table IV). The main reason for homopolymer formation is the presence of impurities capable of reacting with metallic cesium to form initiators for the polymerization of ethylene oxide. A yield of 10% of PEO was obtained by first reacting purified THF with a metallic cesium mirror and then carrying out the subsequent steps as for the preparation of grafts, but in absence of the aromatic polymer.

4. Mechanical Properties

The modulus–temperature curves for the PEO, PVB, and PVN homopolymers are shown in Figure 11. As PEO is heated, at first the modulus decreases gradually in a way characteristic of slow melting in crystalline polymers, until about 65°C. a sharp melting point is reached. The length of the plateau which extends beyond the melting temperature depends on the molecular weight of the polymer. Both PVB and PVN exhibit a constant glassy modulus for low temperatures, and then go through the transition region rather rapidly, as expected for amorphous polymers. It is to be noted that PVB, although having lower molecular weight (450,000 vs. 1,000,000), exhibits a slightly higher T_g than PVN (ca. 154 vs. 148°C.).

The curve for PVB (curve *1*) is reproduced in Figure 12 along with those for two PVB–PEO grafts (curves *2* and *3*), a block (curve *4*), and a blend (curve *5*). The two-component systems exhibit two transitions, one corresponding to the melting of PEO (ca 65°C.) and the other to the glass transition of PVB (130–150°C.). This behavior is similar to that of polystyrene–butadiene blends,[12] but in the presence of appreciable amounts of low molecular weight PEO, only the first transition is observed. The modulus in the intermediate zone 65–130°C., is proportional to the PVB content and is at a level characteristic of leathery behavior. For high molecular weight PVB (curve *2*) a plateau is exhibited, whereas for low molecular weights the modulus gradually decreases (curve *3*). This is not surprising, since PVB is now imbedded in liquid PEO and its mobility should depend primarily on the extent of entanglement with its own species. The latter in turn depends on the molecular weight of PVB. The extension of the PVB chain at both ends in the block polymer sufficiently in-

creased entanglement for the system to exhibit a plateau, although the molecular weight of the PVB portion is only about 60,000. Differences between blends and grafts are not apparent. Qualitative observations, however, indicate that the modulus in the leathery zone relaxes at a faster rate for blends than for grafts. More quantitative observations of time–temperature-dependent behavior are planned in order to assess these differences.

For the PVN–PEO systems (Fig. 13) the modulus–temperature curves exhibited a very unusual behavior. A "well" was observed in the intermediate zone, instead of a plateau. Past the minimum of the well the modulus rises until a maximum is reached at about 120°C., and then decreases as the specimen goes through the transition of PVN. This behavior is exhibited by both blends and grafts, although the well is shallower for the latter. Also, in order to follow the equilibrium curve the temperature had to be changed more gradually for grafts than for blends. Again this strongly suggests markedly greater mobility of chain motions in blends than in grafts.

Although the exact reason for the well behavior is not known, certain experimental observations may be used to offer a plausible explanation. At room temperature the specimen is opaque. As the PEO melts (>65°C.) the specimen becomes transparent, but on further temperature increase (about 80°C.) becomes opaque again. This indicates that at first PVN dissolves in PEO, but as the temperature increases it starts to precipitate out, thus raising the modulus by acting as a filler. Once a specimen had been exposed to a temperature of 120°C. the well behavior is lost, and a behavior similar to that of the PVB systems is exhibited, as illustrated in Figure 14, where the modulus curve of a preheated specimen is shown together with the original curve.

The test specimens are molded at temperatures (100–110°C.) below T_g of PVN, and since the molding powder was obtained by precipitation at room temperature with a nonsolvent from a relatively dilute solution, it follows that the PVN chains are "frozen" in a compact configuration characteristic of the conditions under which they were precipitated. Visual observations indicate that PVN chains in this configuration exhibit maximum solubility in melted PEO at about 65°C. Once the temperature of about 120°C. is exceeded, PVN can uncoil and entangle with the surrounding chains from both PEO and other PVN segments. The exact temperature range depends on both composition and molecular weight. These considerations are consistent with the observed dependence of crystallinity on thermal history. When molded specimens were examined with polarized light, crystalline PEO spherulites could be seen before but not after heating above 120°C.

The factors needed for the well behavior to be exhibited must be quite critical and appear to be related to the thermodynamics of the two-component system. The phenomenon almost certainly depends on the phase relations between PEO and the aromatic system. Although we still lack

data on this point, it is significant that dimethoxyethane, an ether structurally similar to PEO, is a markedly better solvent for PVB than for PVN, and this is consistent with the fact that none of the PVB systems exhibited the unusual "well" phenomenon.

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Synopsis

The aromatic moieties of vinyl polymers such as poly-4-vinylbiphenyl and poly-2-vinylnaphthalene react in solution with alkali metals to form colored charge-transfer complexes. These polymers, referred to as polyradicalanions, initiate the polymerization of ethylene oxide by bond formation, thus leading to the formation of graft polymers. The polyradicalanions, however, may degrade at ambient temperature into polymeric anions. Therefore, to prepare graft polymers one has to select suitable polymer systems as well as reaction conditions which minimize the degradation process. Graft and block copolymers having poly-4-vinylbiphenyl or poly-2-vinylnaphthalene backbones and polyethylene oxide branches were prepared, and the properties of these compared to those of homopolymers and blends. The preparations were characterized by their solubility behavior as well as by chemical and spectral analyses. The mechanical properties were investigated by means of torsional modulus vs. temperature measurements. The reaction mechanisms and relative stabilities of the various species are discussed in terms of molecular orbital calculations. For the poly-2-vinylnaphthalene grafts and blends the modulus exhibited a minimum at about 65°C. A tentative explanation is offered for this phenomenon.

Résumé

Les parties aromatiques des polymères vinyliques tels que le poly-4-vinyl-biphényle et le poly-2-vinylnaphtalène réagissent en solution avec des métaux alcalins pour former des complexes colorés à transfert de charge. Ces polymères, appelés anions polyradicalaires, initient la polymérisation de l'oxyde d'éthylène par formation de liens, conduisant ainsi à la formation de polymères greffés. Les anions polyradicalaires cependant, peuvent se dégrader à température ambiante en anions polymériques. Dès lors, pour préparer des copolymères greffés, il faut choisir des systèmes polymériques adaptés ainsi que des conditions de réaction qui minimisent le processus de dégradation. On a préparé des copolymères greffés et séquencés ayant comme chaîne principale le poly-4-vinylbiphényle ou le poly-2-vinylnaphthalène et comme greffons de l'oxyde de polyéthylène et leurs propriétés sont comparées à celles des homopolymères et des mélanges.

Les produits préparés ont été caractérisés par leur solubilité ainsi que par analyse chimique et spectrale. Les propriétés mécaniques ont été étudiées au moyen de mesures du module de torsion en fonction de la température. Les mécanismes des réactions et les stabilités relatives des différentes espèces sont discutés en termes de calculs d'orbitales moléculaires. Pour les poly-2-vinylnaphtalènes greffés et en mélange, le module présente un minimum aux environs de 65°C. On essaie de donner une explication à ce phénomène.

Zusammenfassung

Die aromatischen Gruppen von Vinylpolymeren, wie Poly-4-vinylbiphenyl und Poly-2-vinylnaphthalin, reagieren in Lösung mit Alkalimetallen unter Bildung gefärbter "charge-transfer"-Komplexe. Diese, als Polyradikalanionen bezeichnete Polymeren starten die Polymerisation von Äthylenoxyd, indem sie eine Bindung zu diesem ausbilden und so zu Pfropfpolymeren führen. Die Polyradikalanionen können aber bei Raumtemperatur zu polymeren Anionen abgebaut werden. Um daher Pfropfpolymere darzustellen, muss man sowohl geeignete Polymersysteme wie auch Reaktionsbedingungen mit geringst möglichem Abbau auswählen. Pfropfund Blockcopolymere mit einer Poly-4-vinylbiphenyl- oder Poly-2-vinylnaphthalin-Hauptkette und Polyäthylenoxyd-Seitenketten wurden dargestellt und ihre Eigenschaften mit denen von Homopolymeren und deren Mischungen verglichen. Die Präparate wurden durch ihr Löslichkeitsverhalten, wie auch durch chemische Analyse und Spektralanalyse charakterisiert. Die mechanischen Eigenschaften wurden anhand von Messungen des Torsionsmoduls in Abhängigkeit von der Temperatur untersucht. Der Reaktionsmechanismus und die relative Stabilität der verschiedenen Stoffe werden auf Grundlage von Molekülorbitalberechnungen diskutiert. Bei Poly-2-vinylnaphthalin-Aufpfropfungen und Mischungen zeigte der Modul ein Minimum bei etwa 65°C. Eine vorläufige Erklärung dieser Erscheinung wird gegeben.

Discussion

N. A. Plate (*Université de Moscow, Moscow, U.R.S.S.*): (*1*) Can you say anything about the kinetics of graft polymerization of your systems compared with the kinetics of polymerization catalyzed by sodium-naphthalene complexes? (*2*) What is the microtacticity of your polymers and did you work with polymers of different microstructure?

A. Rembaum: We have observed that when using sodium as the counter-ion the propagation step is very slow even at 100°C. By the use of a well defined cesium concentration, the graft polymerization is practically over within thirty minutes at 0°C., we did not study the detailed reaction kinetics.

M. Gole (*Institut National des Sciences Appliquées, Lyon, France*): Nous avons travaillé en collaboration avec Corbière et Rempp dans le même domaine depuis trois ans et les résultats que nous avons obtenus sont très semblables à ceux de Rembaum. Je voudrais seulement poser quelques questions pratiques: (*1*) Quels sont les traux de sodation obtenus? (*2*) La dégradation est fonction de la température, est-elle aussi fonction du taux de métallation?

A. Rembaum: The extent of electron transfer from the alkali metal to the aromatic polymer depends on the reaction time and also on the molecular weight and polymer concentration. We found it difficult to form polyradicalanions in concentrated and viscous solutions. Using longer reaction times and more dilute solutions, a high alkali concentration may be achieved. Our polymer contained between 3 to about 30 mole-% of alkali metal.

Teh Fu Yen (*Mellon Institute, Pittsburgh, Penna.*): The positions of bond formation for the graft polymer are consistent with our observation of those of the polymers containing aromatic hydrocarbons prepared by condensation with formaldehyde. In the case of α-methyl naphthalene, the propagation is through 5,8. In the case of the β-isomer, the

propagation is through 1,5. We also observed a shift to higher wave length of the UV-visible spectra of those polymers when compared to those of the parent hydrocarbons.

A. Rembaum: It is very gratifying to hear this.

P. Rempp (*C. R. M., Strasbourg, France*): Did you carry out systematic determinations of the molecular weight of your polymeric system, as a function of their degrees of metallation?

A. Rembaum: We investigated the rate of polymer degradation by viscosimetry as a function of sodium concentration and temperature. We followed the changes of absorption intensities in the visible and the decrease of the intensity of the electron spin resonance signal with time. We have also isolated polymer samples after reaction with a known amount of sodium at different times and determined their molecular weight by light scattering or viscosity measurements.

M. Goutiere (*France*): (*1*) Quelle est la façon de désactiver le polyvinylnaphtalene métallé? (*2*) Pour notre part nous avons utilisé le méthanol et nous avons observé une légère réticulation. Dans le cas- d'un polyvinyl naphtalène de haute masse moléculaire cette réticulation s'explique par le fait que la désactivation transforme un noyau naphtyle en dehydro-naphthle, et que celui-ci est nitrable par le naphtalène sodium restant.

A. Rembaum: We used methanol or methyl iodide for the termination reaction and did not observe any crosslinking in either case. Your observation of insoluble polymer formation may be due to the high sodium concentration which could lead to dianions rather than to radical anions.

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Preparation and Characterization of Some Cellulose Graft Copolymers. Part II

V. STANNETT, J. D. WELLONS, and H. YASUDA, *Camille Dreyfus Laboratory, Research Triangle Institute, Durham, North Carolina*

In Part I of this series[1] a number of methods were described to separate and characterize various graft copolymers of cellulose and cellulose acetate. The cellulose acetate–styrene graft copolymers were found to be particularly amenable to rather simple separation and characterization methods and were selected for a more detailed study. The graft copolymerizations to be reported in this paper were carried out entirely using the mutual radiation method with gamma rays from a Co^{60} source. The variations of yield of true graft, length of side chains and efficiency of grafting have been studied as a function of dose, dose rate, swelling of the substrate and change of swelling medium. In addition, a number of preparations have been made in solution and the graft copolymers characterized.

EXPERIMENTAL

The styrene and solvents used were all distilled under vacuum before use. Cellulose acetate of 1.75 degree of substitution and of viscosity-average molecular weight of about 55,000 was used for this study. It was obtained from the Eastman Kodak Company. The films were cast from a solution in 70% acetone, 20% 2-ethoxyethanol, and 10% water mixture and dried under vacuum at 45°C.

The heterogeneous preparations were carried out in Pyrex tubes, the films and solvent–monomer mixture degassed three times and sealed under vacuum. The solution preparations were treated in the same manner. With very viscous solutions the cellulose acetate and monomer solution were degassed separately and then mixed and dissolved under vacuum.

The radiations were carried out at about 25°C. at a dose rate of 340,000 rads/hr. in the North Carolina State College, Raleigh, N. C., Gammacell. A few irradiations at a lower dose rate were conducted at the State University College of Forestry, Syracuse, N. Y.

The grafted products were separated in the following manner. The grafted films were washed first in benzene, then in a 55:45 acetone–water mixture. The infrared spectra of both extracts were checked to determine if any graft copolymer had been removed. The extractions were then repeated and the residue considered as graft copolymer. Occasional sam-

TABLE I
Heterogeneous Grafting Experiments

Monomer–solvent mixture	Film thickness, mm.	Dose rate, r/hr.	Total dose, Mrad.	Increase in weight		Composition of graft		Efficiency of grafting		[η]	M. W. of PS side chains	M. W. of PS produced in solution
				Actual, %	Due to true graft, %	CA, %	PS, %	CA, %	PS, %			
90 S–10 DMF	0.025	7,650	0.45	183.0	93.6	13	87	13.6	51.8	6.65	4,200,000	—
	"	21,200	0.95	147.0	45.0	27	73	16.7	30.5	5.80	3,500,000	—
	"	340,000	1.0	13.9	6.2	—	—	—	—	—	—	70,000
	"	"	10.0	33.7	—	—	—	—	—	—	—	"
	0.0025	"	1.0	60.8	51.2	22	78	11.1	84.1	3.81	1,945,000	"
	"	"	10.0	169.5	157.4	20	80	34.2	92.9	2.90	1,338,000	"
80 S–20 DMF	0.025	"	1.0	22.9	17.2	30	70	4.0	75.3	2.42	1,044,000	61,000
	"	"	10.1	64.1	37.8	34	66	19.8	59.1	1.45	518,000	"
	0.0025	"	1.0	11.1	—	—	—	—	—	—	—	"
	"	"	10.0	67.2	37.1	41	59	21.5	55.3	0.68	184,000	"
95 S–5 pyridine	"	"	"	79.9	57.3	12	88	7.9	71.8	0.78	220,000	74,000
90 S–10 pyridine	0.025	"	"	53.4	34.0	53	57	19.2	63.7	0.84	245,000	72,000
"	0.0025	"	"	104.7	103.2	34	66	13.6	98.5	1.91	755,000	"
80 S–20 pyridine	0.025	"	"	111.9	92.7	29	71	17.1	90.9	2.28	962,000	66,000
"	0.0025	"	"	79.9	73 7	29	71	62.4	92.2	2.11	865,000	"
"	"	"	"	67.7	65.2	34	66	39.2	96.3	—	—	"
70 S-30 pyridine	"	"	"	17.5	17.0	61	39	31.0	97.1	0.67	181,000	59,000
"	0.025	"	"	23.1	23.1	55	45	28.3	(100)	0.91	272,000	"

ples were double-checked by dissolving in dimethylformamide and precipitating in benzene and then repeating with the aqueous acetone mixture; virtually complete extraction was found to have taken place in every case examined. The increase in weight after the first benzene wash was recorded and is equivalent to the per cent grafting often reported in grafting studies. The difference between this value and the true grafting yield can be seen in Table I. The grafts prepared in solution were isolated by pouring into methanol, filtering, washing with methanol, and drying under vacuum. The dry polymer was then extracted with benzene to remove homopolystyrene and the residue further extracted with the acetone–water mixture. The two extractions were then repeated, the product dried under vacuum and weighed.

The hydrolysis of the graft copolymers was achieved by first swelling about 1 g. in a mixture consisting of 70% acetone, 25% dimethylformamide, and 5% water. A 50-ml. portion of 72% sulfuric acid was then added and left for 2 hr. at room temperature; 500 ml. of water was then added, and the mixture refluxed for 5 hr. after first boiling off the acetone. The remaining polystyrene was then freeze-dried from a benzene solution. The efficacy of the method was checked by using physical mixtures of polystyrene and cellulose acetate.

The intrinsic viscosities were determined in toluene at 25°C. and converted to viscosity-average molecular weights by the formula of Fox and Flory:[2]

$$\log M = \frac{4.010 + \log [\eta]}{0.73}$$

This replaced an earlier formula used in the previous paper of this series.

RESULTS AND DISCUSSION

The previous paper discussed only heterogeneous preparations where the cellulose acetate was grafted in the form of films which maintained their structure throughout the grafting process. In this work some preparations were also made in which the cellulose acetate was completely dissolved in the monomer–solvent mixture. At the end of the grafting reaction these solutions always became turbid but did not separate into two layers except in a few cases, not reported here, where low dose rates leading to high molecular weight side chains were produced. The considerations involved in the film or heterogeneous grafting are somewhat different from those encountered in solution grafting, and the two sets of results will therefore be discussed separately.

Heterogeneous Grafting

All the results to be discussed have been brought together and presented in Table I to avoid unnecessary repetition. In this way the complex interrelationships can be more easily compared. Since only a fixed dose rate

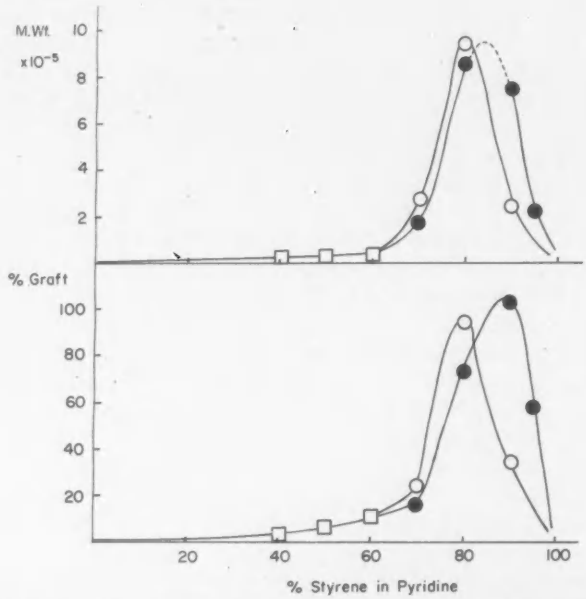

Fig. 1. Per cent grafting and molecular weight of side chains as a function of pyridine content at dose of 10 Mrads at 340,000 rad/hr. at 25°C.: (○) 0.025 mm. thick film; (●) 0.0025 mm. thick film. Values below 60% pyridine are for solution polymerization.

source was readily available only a few comparisons at different dose rates have been made. It can be seen, however, that on increasing the dose rate nearly fiftyfold the rate of grafting only changed from 1.6 to 2.1%/hr. The yield per megarad of radiation fell correspondingly from 207% to only 6%. These results were obtained with 0.025 mm. (1 mil) film thickness; when the thickness was reduced to one-tenth of this value the rate of grafting increased tremendously at the high dose rate but the yield per megarad never reached the low dose rate value.

These effects are readily explained assuming a diffusion controlled growth mechanism and have been discussed at some length by Chapiro[3] in consideration of other systems. If the dose rate is high, sufficient monomer cannot diffuse into the interior of the film and the radicals terminate with little or no chain growth. With thinner films these effects diminish and a greater overall yield of graft is obtained. At very low dose rates no thickness effects should be observed and with very thin films no dose rate effect should be felt except at extremely high dose rates.

The molecular weights of the polystyrene side chains are always many times larger than the homopolystyrene concurrently produced in the monomer solution. This is a clear indication of the tremendous gel effect found in heterogeneous grafting and has been reported and discussed previously.[1]

These high molecular weights lead to the high grafting yields found in heterogeneous systems compared with solution grafting. It is apparent, however, that the diffusion effects on growth and on termination can act in opposite directions. Thus, on increasing the swelling of the films at a fixed thickness the yield of graft can actually drop since, simultaneously, the growth process is enhanced but the rate of termination also increases.

Thus, with thin films, the results in Table I show that on increasing the solvent content of the monomer mixture the yield of graft decreases considerably, both with dimethyl formamide and pyridine. The molecular weight of the grafted side chains is seen to decrease correspondingly. With the thicker films the yield first increases with increasing swelling and then decreases, the molecular weight following suit; these results are shown graphically in Figure 1. With pure styrene monomer and dry cellulose acetate of this grade no measurable grafting took place. Other kinetic effects must also be involved, such as the decrease in the monomer content as the solvent concentration is increased and the role of solvent radicals diffusing into the film from the liquid phase and terminating the growing chains.

It will be shown later in this paper that pyridine is a solvent with considerably reduced radical yield on radiolysis compared with dimethyl formamide. It also has reduced solvent power; for example, the intrinsic viscosity of the cellulose acetate is 1.0 in a 70:30 pyridine–α-methylstyrene mixture compared with 1.15 in a corresponding solution with dimethylformamide and α-methylstyrene. It is interesting to compare, therefore, the effects on the grafting reaction of substituting pyridine for dimethylformamide. With thin films, where diffusion control should be of less importance, dimethylformamide gives much greater yields of graft than pyridine in 10% solution, but the situation is reversed with 20% solutions. Here the swelling is very high with dimethylformamide and the grafted side chains are only three times greater than the corresponding solution homopolystyrene. It would seem, as would be anticipated, that the effect of diffusion control on the termination step persists after the growth rate is normal. With the thicker films the yield is increased by increasing the per cent of either solvent; however, pyridine appears to be more effective than dimethylformamide. In all cases the yields and the molecular weights increase and decrease together, in line with the reasoning outlined earlier. Since there is virtually no change in radical production on changing from 10 to 30% pyridine, it is to be expected that the changes in yield are mainly due to molecular weight differences.

The participation of the cellulose acetate in the grafting process was remarkably low in the experiments reported earlier. This was partly due to the low degrees of swelling used and also to the small total doses used in view of the low dose rate source available at that time. Both conditions are rectified in this work and with 10 Mrads up to 60% of the cellulose acetate was utilized in the best case. Parallel degradation experiments[4] showed only minor changes in the viscosity average molecular weight of

the cellulose acetate at the same total dose. These results strongly suggest that graft rather than block polymers are formed.

The advantages and disadvantages of the heterogeneous method are obvious from the results summarized in Table I. The attractively large yields obtained are mainly the result of the high molecular weight of the side chains and considering the comparatively low molecular weight of the substrate lead to somewhat disproportionate products. The diffusion-controlled nature of the grafting process leads undoubtedly to wide molecular weight distributions of the side chains and also to some lack of reproducibility. The extent of this latter difficulty can be seen in the duplicate preparations carried out in the 80:20 styrene–pyridine solution. One of the major objectives of this study was to prepare quantities of well defined grafts in a reproducible fashion for property studies. It was decided, therefore, to also undertake some preparations in solution and the results of this study will now be reported.

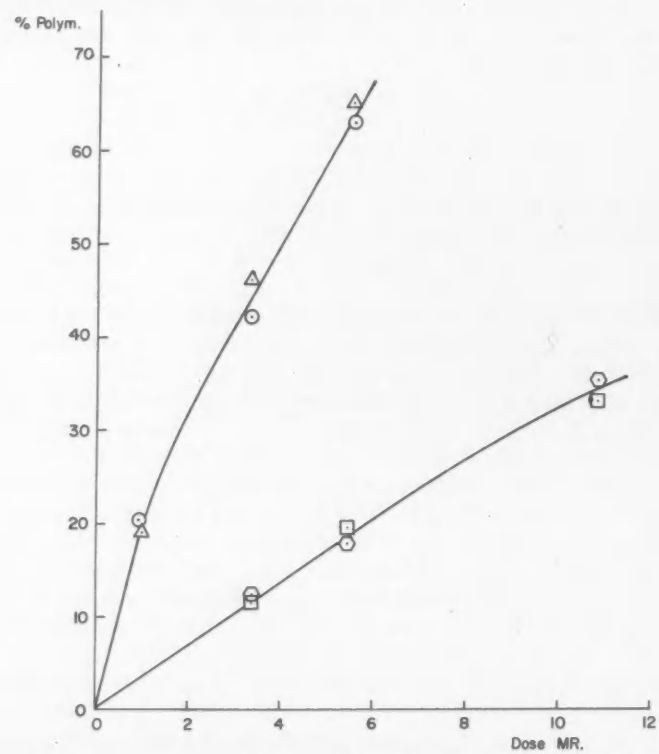

Fig. 2. Solution polymerization of styrene in presence of cellulose acetate at 25°C. with a mixture of 3.5 g. cellulose acetate, 70 cc. dimethylformamide, and 30 cc. styrene: (⊙) 8,300 rad/hr., 33% acetyl value; (△) 8.300 rad/hr., 38% acetyl value; (⬡) 340,000 rad/hr., 33% acetyl value; (⊡) 340,000 rad/hr., 38% acetyl value.

Solution Grafting

Some initial experiments were conducted in dimethyl formamide solution at two widely different dose rates. The polymerization data are presented in Figure 2. The rates of polymerization were found to be 8.79 $\times 10^{-6}$ and 1.23 $\times 10^{-6}$ mole/l. sec. at 340,000 and 8,300 rads/hr., respectively. The ratios of the rates to the square roots of the dose rates were calculated as 0.015 and 0.0135, respectively, showing that the normal square root dependence holds. The viscosity-average molecular weights, on the other hand, were 13,000 and 40,000, showing a lesser dependence on dose rate. However, number-average molecular weights would need to be directly measured to investigate this point further. When the resulting polymers were analyzed it was found that only a very small proportion of graft copolymer was obtained. This was undoubtedly due to the large amounts of homopolymer initiated by radicals resulting from radiolysis of the solvent. Because of its more stable conjugated structure it was thought that pyridine might be a more suitable solvent. The results obtained with this solvent compared with those with dimethylformamide

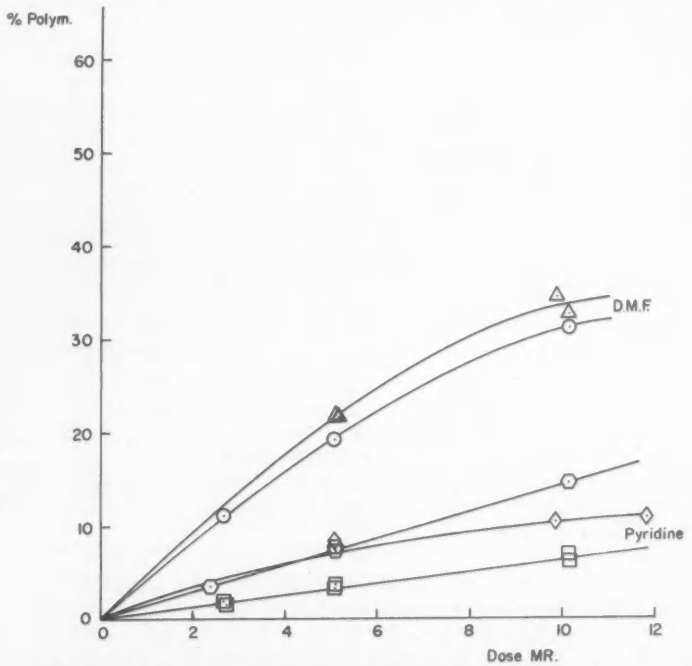

Fig. 3. Solution polymerization of styrene at a dose rate of 340,000 rad/hr., at 25°C. in a mixture of 70 cc. solvent and 30 cc. styrene: (⊙) DMF, no cellulose acetate; (△) DMF, 10% cellulose acetate, 33% acetyl added; (⊡) pyridine, no cellulose acetate; (◇) pyridine, 10% cellulose acetate added; (⬡) pure styrene.

are shown graphically in Figure 3 and illustrate the advantages of this solvent change. It should be pointed out that common solvents for cellulose acetate, polystyrene, and their graft copolymer are very rare, and that the results were therefore particularly gratifying. The remarkably low radical yield from pyridine is of considerable interest in the field of radiation chemistry and has been investigated further, using simple binary mixtures of pyridine and styrene and dimethyl formamide and styrene. The results

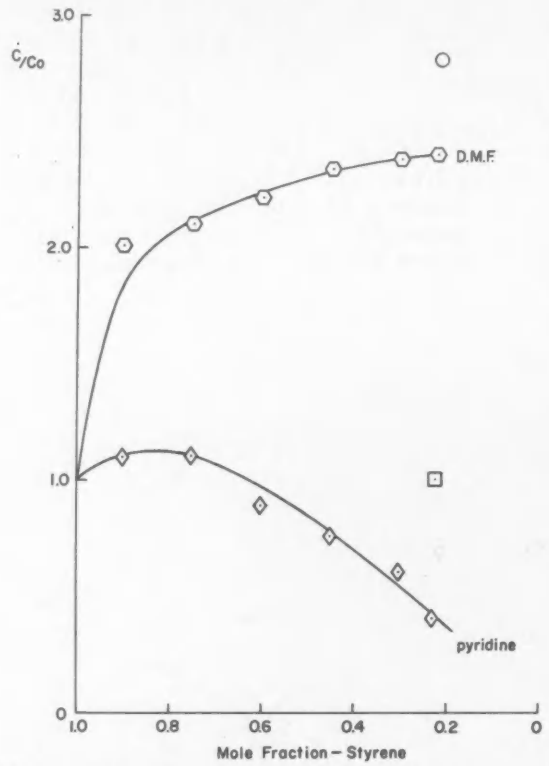

Fig. 4. Relative conversion rates as a function of mole fraction of styrene at a dose rate of 340,000 rad/hr., at 25°C. (○), (⊡) denote corresponding values with 10% cellulose acetate (33% acetyl) added.

are presented in Figure 4 in the manner introduced by Chapiro,[3] where the following kinetic expression is developed:

$$\frac{C}{C_0} = \left[\frac{1}{m + (1 - m)\, V_s/V_m}\right]^{1/2} [1 + \phi_{rel}\,(1 - m)/m]^{1/2}\, m^{1/2}$$

where C and C_0 are the percentage conversion per unit time for the solution and pure monomer, respectively, m is the mole fraction of monomer, V_s

and V_m are the molar volumes of the solvent and monomer, respectively, and ϕ_{rel} is the ratio of the rate constants of free radical production from the solvent and monomer. If energy transfer effects are absent, the curves should be fitted by a single value of ϕ_{rel}. Actually, as shown in Table II, both solvents have variable values showing considerable energy transfer effects. The molecular weights of the corresponding polymers were somewhat erratic, and the values included in Table II are only average values. They do show, however, the expected lower molecular weights obtained with dimethylformamide, the solvent giving the highest rate of radical production.

TABLE II
Relative Rates of Radical Production

Solvent	Mole fraction styrene	C/C_0	M. W.[a]	ϕ_{rel}	Calcd. G_s[b]
Pyridine	1.00	1.00	80,000	—	—
	0.90	1.10	72,000	2.6	0.19
	0.75	1.10	64,500	1.5	0.33
	0.60	0.89	55,000	0.2	0.10
	0.45	0.76	46,000	0.05	0.04
	0.30	0.60	27,000	0	0
Dimethylformamide	0.90	2.01	64,000	30.1	2.30
	0.75	2.10	58,000	13.2	3.04
	0.60	2.22	41,000	9.2	4.24
	0.45	2.34	28,000	7.3	6.11
	0.30	2.38	17,000	5.8	9.17

[a] Viscosity-average.[2]
[b] Assuming $G_m = 0.69$.

Number-average molecular weights would be needed to analyze the molecular weight data further. It should be emphasized that the equation used to calculate ϕ_{rel} is based on the conventional kinetic scheme with termination by the combination of two growing chains. The high dose rate used may have led to some termination by primary radicals. Chain transfer effects have also been neglected, and the G values for radical production from the two solvents should be treated with some reserve.

The relative conversions obtained in the presence of 10% cellulose acetate are included in Figure 4 and, together with the data in Figure 3, give an indication of the considerable proportion of homopolymer which accompanies the grafting reaction in solution. Even with pyridine the yield of graft at 10 Mrads was only about 25% of the total of polymer. Furthermore, the low molecular weight of the side chains and the homopolymer made the separation procedures more difficult. It was not possible, therefore, with the solution polymerizations to make the quantitative breakdown of yields and efficiencies carried out with the heterogeneous preparations. However, the graft copolymers can be separated from the

two homopolymers and their compositions determined by hydrolysis. The results obtained from a series of preparations at 10 Mrads are summarized in Table III. It can be seen that the molecular weights of the side chains were all somewhat higher than the homopolymer, perhaps indicating a local gel effect; turbid solutions were always obtained after the grafting procedure. The products at 10 Mrads consisted of approximately one grafted polystyrene chain per cellulose acetate molecule.

TABLE III
Graft Copolymers Produced in Solution at 25°C.[a]

Styrene–pyridine ratio	Composition of graft		M. W. side chains	M. W. homopolystyrene	Approx. no. of side chains CA molecule[b]
	CA, %	S, %			
30:70			—	15,000	—
40:60	69	31	24,000	19,000	1.0
50:50	66	34	31,000	25,000	0.9
60:40	61	39	39,000	35,000	0.9

[a] Dose rate 340,000 rads/hr., total dose 10 Mrads.
[b] Calculated from the viscosity-average molecular weights.

The solubility of the graft copolymers in pyridine makes it possible to carry out a quantitative removal of the acetate ester groups by alkaline hydrolysis leading to the preparation of the corresponding cellulose–styrene graft copolymers. Since grafted side chains attached to the ester group will also be removed by the alkaline hydrolysis these may be extracted with benzene. In this way the ratio of side chains attached to the main cellulose backbone to those attached to ester groups may be determined. These measurements have been carried out on a sample of graft copolymer prepared in 50:50 styrene–pyridine solution. It was found that 22.4% of the grafted polystyrene was removed by the alkaline hydrolysis or 77.6% of the side chains were attached to the main cellulose backbone. Similar evidence that a large proportion of the side chains are attached to the main cellulose chain was also presented in the first paper of this series.

The solution method, in spite of the comparatively poor yields, is believed to be the most suitable method for reproducibly preparing well defined graft copolymers. A number of large-scale preparations have been carried out at two widely different dose rates. These products are presently being used for further property studies and will be reported shortly.[4]

We would like to thank Mrs. Jane Graper for her help with the experimental work.

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We would also like to thank the U. S. Army Research Office (Durham) for their support of a part of this program.

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Synopsis

The methods of separation and characterization of cellulose graft copolymers which were developed earlier have now been applied in some detail to the cellulose acetate–styrene grafting system. Both heterogeneous and solution graftings have been carried out by the mutual radiation technique. The yields and molecular weights of the side chains have been shown to be mutually dependent and governed by the interplay of diffusion controlled growth and termination steps. The dependence of the molecular weights on the dose rate and film thickness has been determined. Solution grafting has been carried out in both dimethyl formamide and pyridine solutions. Pyridine has been shown to be highly suitable for solution grafting since it has a remarkably low radical yield on radiolysis. The proportions of grafted polystyrene which are attached to the backbone and ester groups of the cellulose acetate have been determined as 77.6% and 22.4%, respectively.

Résumé

On a appliqué en détail sur le système de greffage, acétate de cellulose–styrène, les méthodes développées antérieurement qui permettent de séparer et de caractériser des copolymères de cellulose greffée. Aussi bien le greffage hétérogène que le greffage en solution ont été menés par la technique de radiation mutuelle Le rendement et le poids moléculaire des chaînes latérales sont mutuellement dépendants, et gouvernés par le jeu interne de la diffusion qui contrôle la croissance et les étapes de terminaison. On a déterminé l'influence de la dose, la vitesse et l'épaisseur du film sur les poids moléculaires. Le greffage en solution a été fait dans les solutions de diméthyl-formamide et de pyridine. La pyridine se prête particulièrement bien aux expériences de greffage en solution à cause des faibles quantités de radicaux pyridiniques formés par radiolyse. Les proportions du polystyrène greffé attaché à la chaîne principale, et aux groupements ester de l'acétate de cellulose sont respectivement 77.6% et 22.4%.

Zusammenfassung

Früher entwickelte Trennungs- und Charakterisierungsmethoden für Cellulosepfropfcopolymere wurden nun eingehend beim Celluloseacetat–Styrol-Pfropfsystem angewendet. Heterogene Aufpfropfung und Aufpfropfung in Lösung wurde nach dem Verfahren mit wechselweiser Bestrahlung ausgeführt. Ausbeuten und Molekulargewichte der Seitenketten standen in wechselseitiger Beziehung und wurden durch das Gegeneinanderspiel diffusionskontrollierter Wachstums- und Abbruchsschritte bestimmt. Die Abhängigkeit des Molekulargewichts von Dosisleistung und Filmdicke wurde ermittelt. Aufpfropfung in Lösung wurde in Dimethylformamid und Pyridin durchgeführt. Pyridin erwies sich wegen seiner bemerkenswert niedrigen Radikalausbeute bei der Radiolyse als Lösungsmittel für die Aufpfropfung als sehr geeignet. Die Anteile des auf die Hauptkette und die Estergruppen von Celluloseacetat aufgepfropften Polystyrols wurde zu 77,6% bzw. 22,4% bestimmt.

Discussion

G. N. Richards (*A. M. F., British Research Laboratory, Reading, Great Britain*): We are doing similar work to that described by Dr. Stannett, but using hydrogen per-

oxide instead of irradiation to initiate grafting of styrene to cellulose. From our rate studies in this system we can fully confirm Dr. Stannett's postulates on the importance of restricted termination-diffusion rate control in solid cellulose. I also have two questions: (*1*) The films used in this work were cast from solution. In view of the known difficulty in removing traces of acetone from secondary cellulose acetate, was any determination of residual solvent carried out on the films used for grafting? (*2*) Is there any measure available of the relative importance of the two possible modes of initiation, viz., by primary radical formation on the cellulose—by attack of solvent derived radicals on the cellulose?

V. Stannett: (*1*) Residual solvent was removed by heating the films for 24 hr. *in vacuo* at 60°C. I quite agree that a small amount of residual solvent may remain but this should not be troublesome once the film is immersed in the monomer solvent mixtures. (*2*) This question was not studied specifically, but the yield of graft was similar in both dimethylformamide and pyridine in spite of the enormously greater yield of radicals from the former solvent. This suggests that direct attack of the cellulose is chiefly responsible.

S. H. Pinner (*B. X. Plastics, Essex, Great Britain*): I can confirm that cellulose acetate is fairly insensitive to degradation by ionizing radiation while in the presence of an unsaturated monomer, as shown in my work on the radiation crosslinking of cellulose acetate plasticized with triallyl citrate, when highly insoluble products were obtained with no signs of degradation down to complete conversion of the triallyl citrate. To avoid stabilisation of the cellulose acetate chain by the monomer it is desired to graft, might I suggest that the monomer be replaced by its polymer. In other words, cellulose acetate and polystyrene (or polyacrylonitrile) could be dissolved in a common solvent, probably dimethyl formamide, and if the solution is irradiated, chain cleavage and reunion will occur, leading to linear block copolymers or grafted side chains depending on the relative preference of each polymeric component for radiation crosslinking or dislinking. Block copolymers made in this way have been claimed in a patent and it appears that the technique of Stannett and Hermans might be very suitable for studying such block copolymers.

V. Stannett: I am very interested to hear the interesting confirmative work of Dr. Pinner with multifunctional monomers. We certainly would like to try a few experiments along the lines Dr. Pinner has suggested.

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Rupture d'une Covalence par Voie Physique dans un Polymère Séquencé

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En initiant la polymérisation de l'acrylonitrile à l'aide de groupes hydroperoxydes portés par un tronc polystyrène, nous avions remarqué[1] que l'on ne forme un polymère séquencé polystyrène/polyacrylonitrile qu'à la condition de s'en tenir à des concentrations d'acrylonitrile faibles (<3 moles/1), donc, apparemment, à des greffons courts. On ne recueille guère qu'un mélange des deux homopolymères si l'on utilise de fortes concentrations d'acrylonitrile dans le but d'obtenir des séquences longues.

Nous avons par ailleurs, eu l'occasion de constater dans quelques cas[2,3] que les polymères séquencés subissent une nette dégradation sous l'action d'un traitement bénin tel qu'une cuisson dans un solvant à l'ébullition, traitement que les homopolymères constitutifs supportent parfaitement.

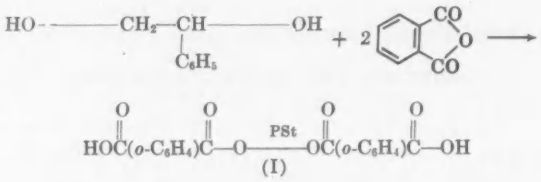
On relève dans la littérature des observations éparses qu'on peut interpréter dans le même sens,[4] mais nous n'y avons pas trouvé d'étude systématique de l'ablation des greffons d'un polymère séquencé par un traitement physique.

PRINCIPE DE L'ÉTUDE

Tout comme au cours des études précédentes nous avons utilisé essentiellement la viscosité intrinsèque $[\eta]$ pour déceler une ablation éventuelle de greffons. D'une facon générale, on sait qu'une baisse de $[\eta]$ révèle une dégradation. Si un traitement, connu pour ne pas modifier la $[\eta]$ de l'un et l'autre des homopolymères constituant un séquencé, en fait pourtant diminuer la $[\eta]$, c'est que cette chute de $[\eta]$ est une propriété spécifique de ce polymère séquencé. On peut envisager que la coupure de chaîne révélée par cette chute de $[\eta]$ se produit sur ou aux alentours de la charnière liant les deux séquences.

Pour être certain d'avoir bien en main des polymères séquencés, et non un simple mélange des deux homopolymères, ainsi que pour pouvoir contrôler l'action du solvant, nous avons préparé des séquencés dont la charnière peut être détruite à coup sûr par un procédé particulier, inoffensif pour les séquences elles-mêmes. Une baisse de $[\eta]$ après ce traitement révèle l'existence de séquencés.

Dans cette idée on a traité par l'anhydride phthalique un polystyrène porteur de groupes OH terminaux:



On passe alors successivement de (I) au chlorure d'acide et au perester butylique tertiaire correspondants. Celui-ci sert à initier la polymérisation du méthacrylate de méthyle. Cette dernière réaction nous fournit un mélange de polystyrène homopolymère (PSt): ———, polyméthylméthacrylate (PMM) ∿∿ et séquencés:

les charnières des séquences étant: soit ∿∿O—CO(o-C_6H_4)COO——— soit ∿∿(o-C_6H_4)COO———au cas où le radical —OCO(o-C_6H_4)COO* se serait décarboxylé.

En tout état de cause les séquences PSt et PMM sont liées par une fonction ester au moins, qui se scinde facilement par un traitement à l'anhydride acétique dont on élimine ensuite facilement l'excès par volatilisation.

Cette méthode n'exige pas une séparation préalable du polymère séquencé, le taux d'abaissement de $[\eta]$ du à l'ablation étant simplement diminué du fait de la présence d'un ballast d'homopolymère.

Il est évident qu'il y a intérêt à simplifier le problème en préparant les séquencés en l'absence complète d'oxygène, pour éviter toute formation de peroxydes. Cette remarque justifie la complication du mode de préparation adopté.

PARTIE EXPERIMENTALE

Préparation du Polystyrène Initiateur

Pour préparer notre polystyrène de départ, porteur de groupes peresters en bout de chaîne, nous procédons en cinq stades successifs.

(*a*) Préparation d'un polystyrène porteur de groupes hydroperoxydes en bout de chaîne, par dégradation oxydative d'un polystyrène de poids moléculaire plus élevé.[5]

On dissout 45 g. de polystyrène de poids moléculaire 260.000 environ et 4,5 g. d'azobisisobutyronitrile dans 300 cc de benzène. Le tout est placé (sous atmosphère d'oxygène) dans une bouteille de 1 litre qu'on fait culbuter pendant 6 hr. dans un thermostat porté à 60°C. Après réaction, on verse la solution benzénique sous forte agitation dans trois à quatre fois son volume de méthanol. Dans certains cas nous avons effectué un fractionnement sommaire pour éliminer les molécules de plus bas DP.

Le produit obtenu que nous désignons par A a une viscosité intrinsèque de $[\eta] = 53,6$ et une teneur en hydroperoxyde de $33,0 \times 10^{-6}$ mole/g.

(*b*) Polystyrène porteur de groupes hydroxyles en bout de chaîne, obtenu par réduction des groups hydroperoxydes sur le polymère préparé ci-dessus.

La solution à 15% de PSt I dans un mélange 1/1 de benzène et de dioxanne (solvant de HI) est additionnée d'acide iodhydrique en solution aqueuse concentrée jusqu'à une teneur d'environ 5%. La réaction s'effectue en milieu homogène à froid en 24 h. Le produit est ensuite débarrassé de l'iodide et de HI par précipitations successives dans le méthanol, puis filtré et séché à l'étuve sous vide à 40°C. Un nouveau dosage des groupes hydroperoxydes sur le polymère B ainsi obtenu, montre que la réduction n'est pas totale puisqu'il subsiste encore, 2.5×10^{-6} mole/g soit 7,5% des hydroperoxydes initiaux. Toutefois ces peroxydes ne sont pas gênants, car ils seront détruits au cours du traitement suivant, sans qu'il y ait à craindre une dégradation notable du polymère.

(*c*) Polystyrène C, porteur de groupes terminaux —O—CO—C_6H_4—COOH.

On chauffe à reflux pendant 24 h une solution benzénique à 10% de B avec de l'anhydride phtalique (3%). Puis, afin d'éviter toute estérification par l'alcool méthylique, on précipite le produit dans le *n*-hexane et sèche à l'étuve sous vide à 40°C.

(*d*) Polystyrène D, portant des groupes —OCO—C_6H_4—COCl.

Le produit précédent est mis en solution à 15% dans du benzène parfaitement anhydre (bidistillé sur sodium), et chauffé à reflux avec du chlorure de thionyle (7%) fraîchement distillé sur huile de lin. Après 24 h de réaction on verse rapidement la solution dans du *n*-hexane. La pâte collante ainsi obtenue est séchée sous vide en présence de pastilles de KOH.

(*e*) Polystyrène E, porteur des groupes peresters OCO—C_6H_4—COOOC-$C(CH_3)_3$.

Le chlorure d'acide (300 g dans 2 litres de benzène) est placé dans un ballon tcherniak et maintenu à une température de 35 à 40°C. Sous forte agitation, on ajoute goutte à goutte, au moyen de deux ampoules, 60 cc de pyridine et 120 cc d'hydroperoxyde de *tert*-butyle. La réaction se poursuit pendant 24 h. Le polymère est ensuite isolé et purifié par trois ou quatre précipitations successives dans le méthanol. Le produit ainsi obtenu est caractérisé par une viscosité intrinsèque de $[\eta] = 43,8$ et une teneur en peresters de 11×10^{-6} mole/g. (Voir également le Tableau I). Le Tableau I décrit quelques produits ainsi préparés.

TABLEAU I

Référence du polystyrène	$[\eta]_0$	Taux de peroxyde *i*, mole/g. $\times 10^6$
PII	37,1	16,1
P III	31,0	23,3
P IV	43,8	11

Préparation des Mélanges Contenant des Séquencés

La réaction de greffage est effectuée en tubes scellés sous vide. Nous décrirons successivement: le remplissage des tubes, la polymérisation proprement dite, l'isolement et le séchage des produits.

Remplissage des Tubes de Polymérisation. Etant donné que lors de la polymérisation nous voulons éviter la présence de toute trace d'oxygène, nous avons mis au point une méthode nous permettant de réaliser le mélange de tous les constituants sous vide, ceux-ci étant préalablement purifiés et parfaitement dégazés. La réalisation en est compliquée du fait qu'il faut mélanger des quantités connues de: polymère initiateur, solvant purifié, et monomère prépolymérisé. La description de l'appareillage utilisé et de son fonctionnement serait trop longue pour pouvoir figurer dans le cadre de cet exposé. Nous dirons simplement qu'on opère en deux stades.

Dans un premier stade on mène parallèlement, dans trois compartiments séparés d'un même appareil construit entièrement en verrerie rodée, les opérations suivantes: degazage, purification du benzène sous vide, et purification du monomère.

Le polymère initiateur est placés en solution benzénique dans un tube à sceller relié à un groupe à vide. On effectue un dégazage par "freezing and thawing" suivi d'un "freeze drying."

Purification du benzène sous vide: partant de benzène bidistillé sur sodium on en parfait le séchage par chauffage à reflux sous vide et en vase clos, sur du $LiAlH_4$. Une distillation sous vide avec séparation d'une fraction de tête améliore encore le dégazage.

Le monomère (styrène ou methacrylate de methyle) est d'abord débarrassé de son stabilisant par lavage à NaOH à 10% puis à l'eau et séché sur de la Driérite. Un chauffage à reflux sous vide et en vase clos, en présence de CaH_2 permet simultanément de réaliser une prépolymérisation et un séchage parfait. Une distillation sous vide avec séparation d'une fraction de tête élimine les dernières traces d'oxygène.

Dans un deuxième stade enfin, on distille toujours sous vide, le monomère et le solvant dans le tube prêt à être scellé et contenant déjà le polymère initiateur dégazé.

Pour permettre de peser le tube laboratoire après l'introduction sous vide de chacun des constituants du mélange réactionnel, on en utilise un modèle spécial muni d'un robinet à vide.

Réaction de Polymérisation. Les tubes scellés chargés sont immergés dans un thermostat réglé à une température voisine de 80 ± 0,1°C. Le milieu étant homogène, il n'est pas nécessaire d'agiter les tubes.

Isolement des Produits. Après réaction, les solutions sont versées sous forte agitation dans trois à quatre fois leur volume de méthanol. Le polystyrène initiateur ayant une forte tendance à rester en solution colloidale non filtrable, il est souvent nécessaire de le floculer par addition de quelques gouttes d'une solution concentrée de KCl.

Le polymère est ensuite filtré, lavé et séché à l'étuve à 40°C. Pendant toutes ces opérations on avait pris soin de ne perdre aucune fraction.

La pesée du produit obtenu, nous permet de déterminer l'augmentation de poids, et par suite le taux de conversion ρ.

Les données numériques concernant les réactions de greffage du PSt et PMM sur du PSt figurent respectivement dans les Tableaux II et III. Tous les greffages ont été faits à 80°C.

Tous ces produits ont été caractérisés par la mesure de leur viscosité intrinsèque $[\eta]_i$.

TABLEAU II
PSt/PSt

Référence du polystyrène engagé	Polystyrène, g	Styrène monomère, g	Benzène, g	Durée, h	Titre en peroxyde du polystyrène i, mole/g. $\times 10^6$	Taux de conversion du styrène ρ, %	Taux x de polystyrène préformé dans le produit final, %
	—	—	—		16,1	—	—
PIIa	3,003	15,8	64,5	8h10	9,3	3.96	82,8
PIIb	4,85	23,3	103,0	15h	6,16	8,97	79,8
PIIc	4,94	26,0	92,3	24h	3,63	12,4	60,4

TABLEAU III
PSt/PMM

Ref du PSt engagé	Polystyrène, g	Methacrylate de méthyle, g	Benzène, g	Durée, h	Titre en peroxyde du polystyrène i, moles/g $\times 10^6$	Taux de conversion du méthacrylate ρ, %	Taux x de polystyrène dans le produit final, %
	—	—	—	—	23,3	—	—
PIIIa	5,015	12,4	82,8	5h50	15,5	14,9	73
PIIIb	5,002	13,7	104,9	11h30	13,8	21,4	62,9
PIIIc	5,003	13,6	95,8	24h15	11,6	32,0	53,4
PIVa	4,988	11,1	118,1	24h	4,5	19,7	69,5
PIVb	4,988	15,2	116,2	24h	4,0	19,9	62,2
PIVc	4,974	32,8	103,8	24h	4,5	21,8	41
PIVd	5,003	46,2	88,3	24h	3,9	22,9	22,2

Caractérisation des Produits

Mesures de $[\eta]$. Une variation de $[\eta]$ est certainement le critère le plus sensible pour détecter la coupure de certaines chaînes dans un mélange. Mais il faut que l'opération au cours de laquelle une dégradation peut éventuellement se produire soit conduite de façon à ce qu'aucune fraction

du polymère ne se perde et qu'ensuite on mesure $[\eta]$ sur un bon échantillon moyen du produit récupéré.

Nous avons obtenu les meilleurs résultats en congelant rapidement une solution benzénique homogène dans l'azote liquide et en éliminant ensuite le solvant par "freeze drying." De cette facon, le produit reste homogène et se met facilement à poids constant.

Chaque fois que nous avons un produit en solution dans un solvant autre que le benzène, on élimine ce dernier par évaporation sous vide afin de pouvoir appliquer le traitement ci-dessus.

Toutes nos mesures ont été effectuées à l'aide d'un viscosimètre Ubbelohde à boule suspendue et à dilution directe, dans un bain thermostaté à 25 ± 0,1°C, le solvant étant du benzène bidistillé. Les résultats sont exprimés en unités C.G.S.

Rupture Spécifique des Chainons Esters. Eu égard aux servitudes rappelées au paragraphe précédent nous avons procédé à la rupture des groupes ester par l'anhydride acétique, en opérant dans le vide pour éviter toute peroxydation ou dégradation par l'air.

Dans un tube muni d'un étranglement, 1 g de polymère est dissous dans un mélange de 50 cc de benzène et de 50 cc d'anhydride acétique. Après dégazage par "freezing and thawing" ce dernier est scellé, sous vide et porté à 80°C pendant 48 h.

Après transvasement dans un nouveau tube, on élimine le solvant et l'anhydride acétique par évaporation sous vide. On reprend à nouveau par du benzène dont l'élimination par "freeze drying" nous laisse un produit spongieux et parfaitement sec dont on détermine la viscosité intrinsèque: $[\eta]_4$.

La preuve que ce traitement n'altère pas les séquences de PMM est fournie par le fait que la $[\eta]$ d'un homopolymère de PMM est restée inchangée au cours du même traitement (429 C.G.S.)

Les chutes de $[\eta]$ observées dans le cas des "séquencées" PSt–PSt (voir tableau IV) et qui sont en accord satisfaisant avec les calculs cinétiques, nous montrent que la rupture des liaisons est effective.

Dosage des Peroxydes. Dans le but de mettre en évidence une relation éventuelle entre le taux de peresters et la chute de viscosité observée dans l'hypothèse où celle-ci serait due à une dégradation oxydative, nous avons dosé systématiquement les peroxydes sur tous nos produits.

La méthode employée est celle de Ueberreiter et Sorge[6] utilisant la leucobase du bleu de méthylène.

Les résultats (i) sont exprimés en mole de groupe —O—O— par gramme de polystyrène perester engagé. (Tableaux II et III).

Etude des Polymères Séquéncés: Traitements aux Solvants

Nous avons essayé un solvant commun aux deux séquences (le benzène), et un solvant de la séquence PMM seulement (l'acétonitrile).

Méthode: 1 g de polymère dissous dans 100 cc de benzène (ou mis en

présence de 100 cc d'acétonitrile) est placé dans un tube à sceller adaptable à un groupe à vide.

Après dégazage par "freezing and thawing" on scelle sous vide et porte le tout à 80°C pendant une durée de 24 h (48 h de traitement donnent le même résultat).

On élimine ensuite le benzène directement par "freeze drying." L'acétonitrile ayant un point de congélation très bas, il est nécessaire de l'éliminer d'abord par distillation sous vide, avant de reprendre le produit au benzène afin de pouvoir le sécher par "freeze drying."

Sur les produits spongieux ainsi obtenus, on détermine à nouveau la viscosité intrinsèque dans le benzène à 25°C.

Les résultats, $[\eta]_2$ après traitement au solvant commun (benzène) et $[\eta]_3$ après traitement au solvant sélectif (acétonitrile) figurent aux Tableaux IV et V.

TABLEAU IV
PSt/PSt

Référence du polystyrène engagé (Tableau I)	$[\eta]_0$ (Tableau I)	Référence du greffé engagé	Viscosite intrinsèque $[\eta]_1$	$[\eta]_2$	$[\eta]_4$	$[\eta]_G$
PII	37,1	PIIIa	50,8	50,8	48,3	113.7
		PIIb	56,8	56,8	49,4	89.7
		PIIc	67,8	67,8	53,3	118.0

[a] $[\eta]_G$ désigne la viscosité intrinsèque moyenne des greffons et se calcule en admettant une destruction complète des charnières esters: $[\eta]_4 = x[\eta]_0 + (1 - x)[\eta]_G$ où x est donné au Tableau II.

TABLEAU V
PSt/PMM

Référence du polystyrène engagé (Tableau I)	$[\eta]_0$ Tableau I	Référence du greffé engagé (Tableau III)	Viscosité intrinséque $[\eta]_1$	$[\eta]_2$	$[\eta]_3$	$[\eta]_4$	$[\eta]_G$
PIII	31,0	PIIIa	47,3	45,5	46,7	41,2	69,0
		PIIIb	58,9	54,4	54,9	50,0	85,0
		PIIIc	67,5	64,2	63,0	55,2	83,0
PIV	45,3	PIVa	63,3	63,3		61,6	98,6
		PIVb	76,9	73,5		72,1	116,0
		PIVc	139,0	132,0		125,0	181,0
		PIVd	180,0	180,0		176,0	238,0

DISCUSSION

Le but de la série d'expérience de greffage de polystyrène (PSt) sur un tronc de polystyrène est double. D'une part elle se propose de montrer que la synthèse proposée forme effectivement du polymère séquencé. Cela

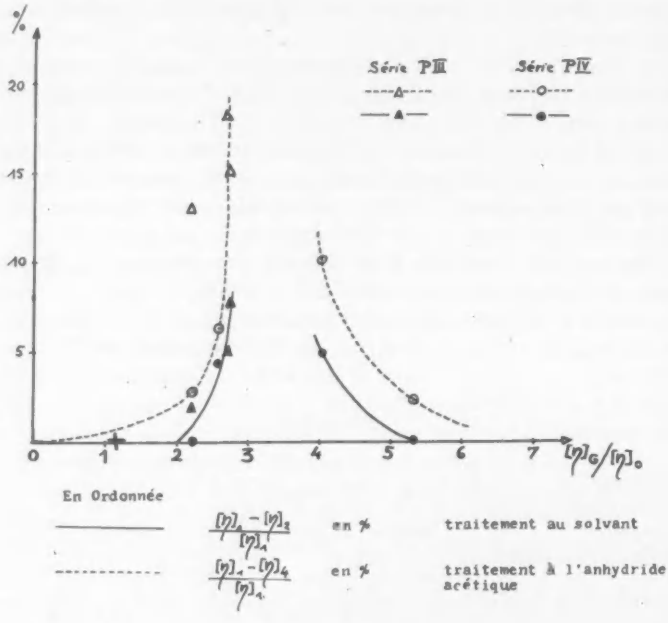


Figure 1.

ressort de la confrontation des chiffres des colonnes 4 et 6 du Tableau IV. D'autre part elle veut prouver que la charnière polyester introduite n'apporte pas par elle-même une fragilité particulière (Tableau IV, colonnes 4 et 5) au polymère et que les groupes peresters n'ayant pas réagi (Tableau II, colonne 6) ne provoquent pas non plus de dégradation.

Etant donné le but de notre étude il fallait que tous ces contrôles soient effectués dans le cas idéal d'un "séquencé" dont les deux séquences sont parfaitement compatibles.

Par ailleurs le Tableau II nous révèle qu'en fonction du temps le taux de transformation ρ croît (colonne 7), que la quantité d'initiateur restant disponible i décroît (colonne 6). Par ailleurs le poids moléculaire moyen du polystyrène formé augmente légèrement (Tableau IV, colonne 7). Tous ces résultats sont conformes à ce que laisse prévoir la cinétique classique; ou peut donc penser que, de même, la taille moyenne des greffons croît avec le taux de conversion.

Les expériences de greffage de polyméthylméthacrylate PMM sur un tronc PSt, résumées dans les Tableaux III et IV peuvent s'interpréter de façon analogue. On y relève la preuve de l'existence de polymères séquencés (Tableau V, colonnes 4 et 7) et des relations analogues entre la durée de l'expérience de greffage, ρ, i (Tableau III) et la viscosité intrinsèque des greffons $[\eta]_G$.

TABLEAU VI
Polystyrène/Polyacrylonitrile

Référence polystyrène engagé (Tableau I)	$[\eta]_0$	Polystyrène engagé, g	Acrylonitrile engagé, g	Diméthyl-formamide, g	Taux de transformation p, %	Taux de polystyrène x dans le produit final, %	Viscosité intrinsèque $[\eta]_1$	$[\eta]_2$	$[\eta]_3$	$[\eta]_4$
PIV	27,8	4,03	14,8	108,4	6,75	80,0	33,5	29,2	29,3	31

Le traitement par un solvant entraîne une chute de $[\eta]$ (Tableau V, colonnes 4–6) inférieure à celle qui résulte de l'ablation de tous les greffons mais qui est sensiblement la même que le solvant soit commun aux deux séquences ou solvant de l'une d'elle seulement.

Ajoutons qu'il ne semble pas que ces dégradations soient dues à l'action des groupes peresters restants puisque dans certains cas (Tableau V, produits PIVa et PIVd) la différence $[\eta]_1 - [\eta]_2$ est nulle malgré un taux de peroxyde restant *i* relativement élevé.

Enfin il semble qu'une chute une chute de $[\eta]$ n'apparaisse qu'à l'intérieur d'un certain intervalle du rapport entre la viscosité intrinsèque $[\eta]_G$ du greffon à celle $[\eta]_0$ du tronc porteur (Fig. 1).

Burnett[10] signale d'ailleurs l'existence d'un domaine analogue à l'intérieur duquel certains paramètres thermodynamiques des copolymères séquencés PSt–PMM présentent des valeurs anormales.

Le rapprochement de ces observations nous inciterait à croire que les chutes de $[\eta]$ sont dues à l'incompatibilité des séquences constituant les copolymères PSt—PMM.

Généralisation

Ce phénomène d'ablation des greffons par un traitement par solvant à chaud a été mis en évidence sur d'autres séquencés.

Sans décrire par le menu les méthodes de préparation des produits engagés nous présentons nos résultats sous forme des Tableaux VI et VII.

A. Copolymères Séquencés à Charnière Ester.

(Polystyrène/polyacrylonitrile). Toutes les viscosités intrinsèques (Tableau VI) ont été mesurées dans la DMF solvant commun aux deux homopolymères et au séquencé. $[\eta]_2$ (Tableau VI) a été obtenu après traite-

TABLEAU VII
Polyisobutylène/PMM

	PIB engagé,	Méthacrylate de méthyle,	Solvant,	Durée,		Viscosité intrinséque		
$[\eta]_0$	g	g	g	h	x, %	$[\eta]_1$	$[\eta]_2$	$[\eta]_3$
33,1	3,80	27,8	Toluène, 129	12	47,5	82,8		80
33,1	3,64	26,7	Toluène, 124	24	42,9	94		92
33,1	3,90	28,6	Toluène 132,5	48	33	106,4		105
33,1	4,62	25	Benzène, 121	48	51,3	167,2	148	144,8

ment (24 h sous vide à 80°) dans la DMF solvant commun; $[\eta]_3$ a été obtenu après traitement (24 h sous videà 80°) dans le benzène solvant sélectif du PSt.

Si la valeur $[\eta]_4$ obtenue après traitement à l'anhydride acétique dans le benzène est supérieure à $[\eta]_2$ et $[\eta]_3$ cela peut être du à une attaque partielle du groupe nitrile par l'anhydride acétique liée à une augmentation de $[\eta]$.

Dans cette catégorie nous évoquerons simplement une série de polysébaçates d'hexane diol greffés de polystyrène dans lequel $[\eta]$ baisse par un traitement au benzène en atmosphère inerte au cas où les deux séquences constitutives sont assez longues.[3]

B. Copolymères Séquencés à Charnière Ether.

(Polyisobutylène/polyméthacrylate de methyle). Les séquencés ont été préparés à 80°C.[1] $[\eta]_2$ (Tableau VII) est la viscosité intrinsèque du produit traité sous atmosphère inerte (24 h à 80°C) dans le benzène; $[\eta]_3$ est la viscosité intrinsèque du produit traité sous atmosphère inerte 24 h à 80°C dans le méthyléthylcétone; x est le taux du mélange obtenu en polyisobutylène.

Dans cette catégorie nous placerons aussi une série de polystyrènes greffés de polyéthylène oxyde dont la viscosité intrinsèque décroît après traitement au cyclohexane à la condition que le tronc polystyrène soit assez long.

C. Copolyméres Séquencés á Charnière C—C

(Polystyrène/polyméthacrylate de méthyle.) Nous avons préparé, à partir d'un polystyrène "vivant" de Szwarc, un séquencé PSt/PMM selon la technique de Rempp.[8] La $[\eta]_0$ du tronc PSt était de 117,0 celle du greffé $[\eta]_1$ de 188,0 et le poids moléculaire de la séquence PMM évalué selon Benoit,[9] de 1.000.000.

Ce produit a été traité à l'abri de l'air à 80°C par le benzène d'une part, par le cyclohexane (solvant du seul polystyrène) de l'autre. On n'a constaté aucune variation de $[\eta]$.

Pour ce produit, la valeur de $[\eta]_G$ peut se calculeuler à partir de la relation

$$[\eta]_G = 5{,}5 \times 10^{-3} M^{0{,}73}$$

On remarque que le point representatif (+) correspondant dans le diagramme de la Figure 1 se trouve dans un intervalle de $[\eta]_G/[\eta]_0$ où l'ablation des greffons semble ne pas se produire.

CONCLUSION

De l'ensemble des observations relatées dans cet article semble résulter que des polymères séquencés à séquences d'une certaine longueur sont assez instables. Comme ces produits supportent aussi mal un traitement par solvant sélectif d'une des séquences qu'un traitement par un solvant commun aux deux, on peut penser que c'est l'incompatibilité foncière des deux séquences qui est la cause de l'instabilité des séquencés.

L'incompatibilité de deux séquences représenterait une énergie suffisante pour rompre une covalence.

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Résumé

Une série de copolymères séquencés polystyrène/polyméthylméthacrylate dont les séquences sont liées par un chainon ester a été préparée. Sur ces produits, il est facile de mettre en évidence la présence effective de polymères séquencés, sans aucune séparation préalable, par une chute de $[\eta]$ à la suite d'un traitement capable de scinder uniquement la liaison ester. Après chauffage à 80°C de solutions de ces copolymères à l'abri de l'air, on a constaté également une chute de $[\eta]$ à condition que les séquences aient une certaine longueur. Il est vrai que les chutes de $[\eta]$ sont inférieures à celles qui résultent de la coupure de la liaison ester. Cet effet a été constaté également sur des copolymères séquencés de nature chimique différente.

Synopsis

Block copolymers of polystyrene and polymethyl methacrylate in which the blocks are connected by an ester linkage were synthesized. On such products the presence of block copolymers can be detected without any purification by a decrease of the $[\eta]$ value after a chemical cleavage of the ester linkage. On the other hand, a decrease of the $[\eta]$ value was observed after heating a solution of such a copolymer with blocks of proper length up to 80°C. in the absence of air. The observed decreases were, however, always smaller than those observed after the chemical cleavage of the ester linkage. One may then conclude that, in favorable cases, this physical treatment will tear off some of the blocks of the copolymer. Other examples of this effect on other copolymers are briefly described.

Zusammenfassung

Eine Reihe von Polystyrol/Polymethylmethacrylat Blockcopolymeren, deren Blocks durch eine Esterbindung miteinander verknüpft sind, wurde hergestellt. An solchen Produkten lässt sich die Anwesenheit von Blockcopolymeren ohne jegliche Fraktionierung durch Spaltung der Estergruppe nachweisen, in Form einer Abnahme der $[\eta]$. Anderseits konnte eine Abnahme der $[\eta]$, nach Erwärmung auf 80° von Blockpolymeren mit Gliedern angepasster Länge in Lösung unter Luftausschluss beobachtet werden, wenn auch diese Abnahme stets geringer als bei der Spaltung ausfiel. Der Schluss liegt daher nahe, dass auch eine rein physikalische Behandlung genügt, um—in günstigen Fällen—eine Ablösung von Blocks zu Stande zu bringen. Weitere Beispiele dieses Effekts bei Blockpolymeren anderer chemischer Zusammensetzung sind kurz beschrieben.

Discussion

P. Lebel (*Kléber-Colombes, Paris, France*): A-t-il été possible de procéder à une étude cinétique du phénomène de scission, et plus particulièrement à l'étude de l'énergie d'activation du phénomène. Il n'est pas certain que l'on aurait là une réponse claire du problème posé mais si le mécanisme est simple, il serait peut-être possible de voir si le facteur qui prévaut est la séparation de phase évoquée à la fin de l'exposé ou si c'est plutot le phénomène de rupture de chaînes à la "charnière" entre le tronc et le greffon.

A. Banderet: Jusqu'à présent nous n'avons opéré qu'à la température de 80°C. dans le benzène pur ou dans un solvant séléctif pur. Dans des conditions expérimentales différentes, les mêmes chutes de $[\eta]$ peuvent être observées à la température ambiante, lorsqu'on précipite une solution de nos copolymères PSt-PMM dans le benzène (solvant commun aux deux séquences) ou dans l'acétonitrile (solvant sélectif du polymethacrylate de methyle).

PROPERTIES OF BLOCK AND GRAFT COPOLYMERS IN THE SOLID STATE

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Propriétés des Copolymères Obtenus par le Greffage de Monomères Vinyliques sur la Cellulose

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La chimie de la cellulose s'occupe actuellement de recherche de procédés qui modifieraient les propriétés de la cellulose native, en vue d'obtenir des propriétés nouvelles, concurrençant les propriétés des polymères synthétiques.

Une des méthodes d'avenir est celle du greffage sur la cellulose de chaines de polymères synthétiques.

Le greffage, comme on le sait, n'est possible qu'après une activation préalable de la cellulose par diverses méthodes chimiques ou physiques.[1–5]

Nous avons greffé divers monomères vinyliques sur la cellulose par irradiation aus rayons. Cette méthode a été très peu employée avec ce matériau. L'influence des conditions expérimentales telles que la concentration du monomère, de la dose d'irradiation, de la température, ne sont pas décrites jusqu'à présent. Dans aucun travail publié on ne trouve d'étude systématique des propriétés des celluloses greffées ainsi obtenues. Il est donc difficile, avec les indications bibliographiques actuelles de régler le processus de greffage pour l'obtention des propriétés désirées de celluloses greffées.

Dans le présent travail, nous n'exposérons que les résultats concernant les propriétés de celluloses greffées. La méthode de leur préparation, ainsi que les méthodes d'analyses de leurs propriétés sont décrites antérieurement.[5,6]

Les résultats obtenus sont réunis dans les Tableaux I et II et dans les Figures 1–5.

Spectres Infra-rouges

Dans les spectres infra-rouges de la cellulose greffée il y a apparition de nouvelles bandes d'absorption caractéristiques des monomères employés (Fig. 1).

Ainsi, dans les spectres de la cellulose greffée avec le méthacrylate ou avec l'acrylate, on observe une bande intense à 1730 cm^{-1}, correspondant aux vibrations du groupe carbonyle. Il est difficile d'apprécier le degré de greffage d'après l'intensité de cette bande. Une augmentation de l'intensité de l'absorption de la bande de vibration du groupe méthylène (1430 cm^{-1}) ce la cellulose est également significative pour ces produits.

TABLEAU I
Quelques Propriétés de la Cellulose Greffée avec l'Acrylonitrile et avec le Methacrylamide

Produit greffé	Dose d'irradiation, $r \times 10^6$	Augmentation en poids, % par rapport au poids de la cellulose	Chaleur de mouillabilité, cal/g	Numéro métrique	Résistance des fibres isolées, g		
					Avant l'enterrement et avant le chauffage	Aprés l'enterrement dans le sol	Aprés le chauffage
Cellulose greffée avec l'acrylonitrile	Contrôle	—	8,25	6160	4,60	2,50	2,60
	0,5[a]	—	8,30	6180	4,48	—	—
	1	—	8,35	6100	4,43	—	—
	0,5[a]	6,9	6,80	5300	4,40	3,82	3,42
	"	10,3	5,10.	4770	4,36	4,00	4,14
	"	29,5	4,30	4280	4,34	4,06	4,20
	1	7,2	6,70	5060	4,56	3,90	3,63
	"	11,0	4,90	4680	4,38	4,05	4,02
	"	33,0	3,60	4150	4,24	4,22	4,25
Cellulose greffée avec le methacrylamide	Contrôle	—	8,25	5120	4,14	2,30	2,35
	1	28,5	15,80	4000	4,00	3,58	2,88
	"	38,4	17,00	3700	4,05	3,56	3,07
	"	56,6	19,50	3340	4,16	4,25	3,30
	"	61,2	21,50	3300	4,00	4,35	3,45
	"	65,2	23,20	3360	4,10	4,29	3,83
	"	68,1	25,80	3100	4,12	4,30	3,94

[a] Cellulose irradiée dans l'eau en l'absence du monomère.

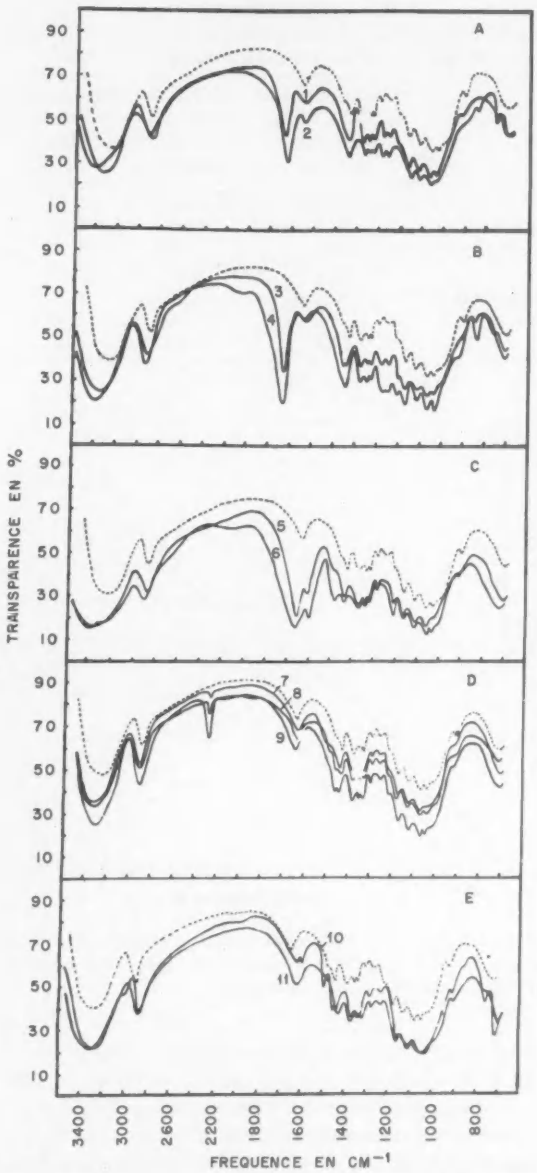

Fig. 1. Spectres infra-rouges de celluloses greffees et de cellulose initiale. Celluloses greffées avec: (*A*) le méthacrylate: (*1*) 20,8%; (*2*) 54,0%; (*B*) méthacrylate de méthle: (*3*) 19,2%; (*4*) 26,0%; (*C*) methacrylamide: (*5*) 28,5%; (*6*) 68,1%; (*D*) l'acrylonitrile: (*7*) 4,6%; (*8*) 7,21%; (*9*) 33,0%; (*E*) le styrolene: (*10*) 12,1%; (*11*) 47,0%. Les chiffres indiquent l'augméntation de poids en % du poids de la cellulose initiale.

TABLEAU II

Quelques Propriétés de la Cellulose Greffée avec le Styrolène et avec l'Acide Methacrylique au (Dose d'Irradiation 1×10^6 R)

Produit greffé	Augmentation du poids, % du poids de la cellulose	Chaleur de mouillabilité par l'eau, cal/g	Résistance des fibres isolées, g	Numéro métrique
	Contrôle	8,25	4,14	5120
Cellulose gréffée avec	12,1	6,53	4,10	4920
le styrolène	25,0	5,15	3,96	4700
	47,0	3,47	3,94	4020
Cellulose greffée avec	8,0	9,70	4,20	4980
l'acide méth-	17,3	10,60	4,17	4210
acrylique	60,0	13,60	4,05	3200

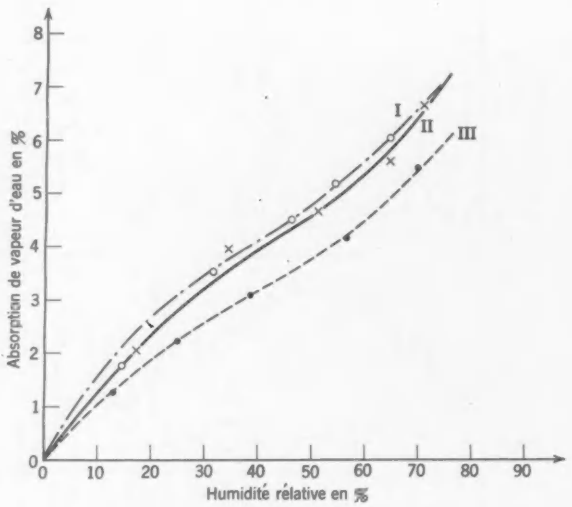

Fig. 2. Absorption de vapeu rd'eau par la cellulose greffée avec le nitrile acrylique (dose d'irradiation 1×10^6 r): (I) cellulose initiale; (II) cellulose greffée, taux, d'azote 1,90%; (III) cellulose greffée, taux d'azote 8,65%.

Dans le cas du greffage par le methacrylate de methyle on observe l'apparition d'une nouvelle bande à 1450 cm.$^{-1}$. Lorsque le taux de greffage augmente, les deux bandes précédentes se superposent en une seule beaucoup plus intense que celle de la cellulose initiale.

Il est difficile d'analyser le spectre obtenu dans la région 1000 à 1300 cm^{-1}, à cause de la superposition du spectre du produit greffé et de celui de la cellulose elle-même. On peut, néanmoins, noter la présence d'une nouvelle bande à 1200 cm^{-1}, qui se retrouve également chez la cellulose greffée par l'amide méthacrylique.

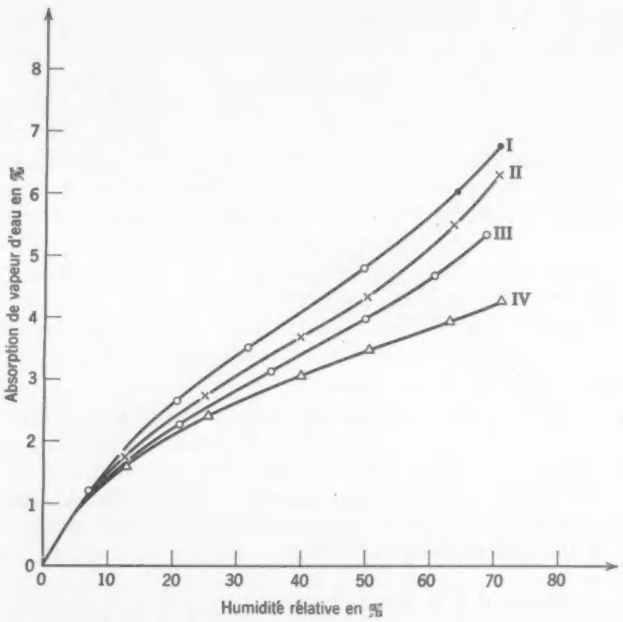

Fig. 3. Absorption de vapeur d'eau par la cellulose greffée avec le styrolene (dose d'irradiation 1×10^6 r): (*I*) cellulose initiale; (*II*) cellulose greffée, augment de poids: 12,1%; (*III*) 25,0%; (*IV*) 47,0%.

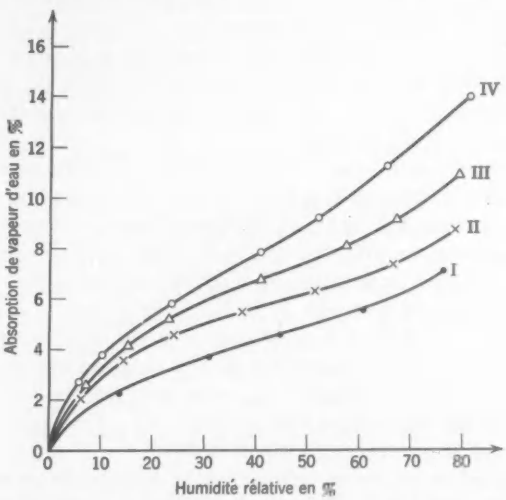

Fig. 4. Absorption de vapeur d'eau par la cellulose greffée avec méthacryliamide (dose d'irradiation 1×10^6 r): (*I*) cellulose initiale; (*II*) cellulose greffée, augment. de poids: 28,5%; (*III*) 56,6%; (*IV*) 68,1%.

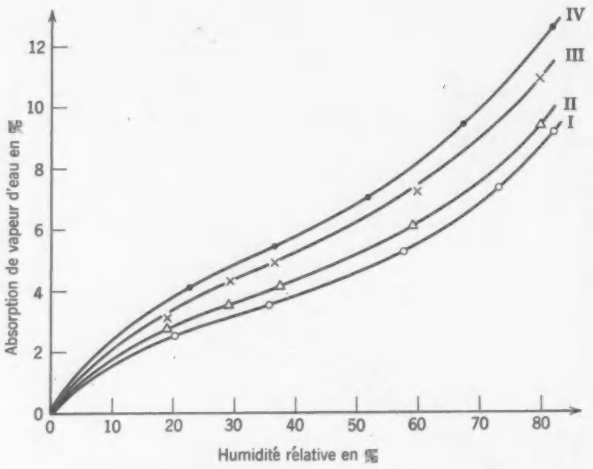

Fig. 5. Absorption de vapeur d'eau par la cellulose greffée avec l'acide méthacrylique (dose d'irradiation 1×10^6 r): (*I*) cellulose initiale; (*II*) cellulose greffée, augment. de poids: 17,3%; (*III*) 60,0%; (*IV*) 70,0%.

Dans la région des faibles fréquences, on remarque l'apparition de nouvelles bandes d'absorption, en particulier à 745 et à 837 cm^{-1} pour la cellulose greffée par l'acrylate de méthyle et à 745 et à 826 cm^{-1} pour la cellulose greffée par le methacrylate de méthyle. L'intensité de la bande commune à 745 cm^{-1} est beaucoup plus forte pour les dérivés obtenus avec l'acrylate que pour ceux avec le méthacrylate; par contre, l'intensité de la bande à 826 cm^{-1} due au méthacrylate de méthyle est plus forte que nel'est celle de la bande voisine à 837 cm^{-1}, due à l'acrylate de méthyle. On peut par conséquent discner entre les deux copolymères greffés au moyen de l'analyse de ces deux bandes.

En ce qui concerne les spectres de la cellulose greffée avec méthacrylamide on constate d'abord une importance dans l'augmentation de l'intensité d'absorption à 3300 cm^{-1}, provoquée par la superposition de la bande d'absorption des groupes hydroxyle de la cellulose elle même et de la bande de vibration du groupe NH_2 d'amide méthacrylique. On observe ensuite un certain déplacement de la bande de vibration du groupe CH (de 2900 cm^{-1} vers 2870 cm^{-1}) et l'apparition de deux bandes intenses à 1663 et 1600 cm^{-1}. La première de ces deux bandes correspond apparemment aux vibrations du groupe C=O de la fonction amide, et la seconde aux vibrations de déformation du groupe NH_2. On note également la présence d'une bande caractéristique à 1475 cm^{-1}, correspondant aux vibrations de déformation du groupe amide méthacrylique et celle d'une bande intense à 1205 cm^{-1}, difficile à interpréter. Cette bande, ainsi que celle de 1663 et de 1660 cm^{-1}, peuvent servir à une détermination du taux du greffage.

La cellulose greffée par l'acrylionitrile possède un spectre dans lequel apparait une bande caractéristique à 2250 cm^{-1}, correspondant aux vibrations du groupe nitrile. Celle-ci peut servir à l'identification de la nature chimique du polymère greffée, ainsi qu'à la détermination du taux de greffage. En outre, la bande observée à 1450 cm^{-1}, est liée apparemment aux vibrations minimes des groupes méthylène de nitrile acrylique.

Dans tous ces copolymères greffés on observe une diminution de l'intensité de la bande de la cellulose à 910 cm^{-1}, ce qui peut être considéré comme une preuve indirecte du greffage sur la cellulose.

Les spectres de la cellulose greffée avec le styrolène accusent des bandes dues à la présence d'un noyau aromatique, en premier lieu à 700 et à 748 cm^{-1} (correspondant aux dérivés monosubstitués du benzène), à 1603 cm^{-1} (due aux doubles liaisons du noyau aromatique) et à 1500 cm^{-1} (due au noyau du benzène). La bande à 1450 cm^{-1} qui est également présente dans le spectre, est liée aux vibrations de déformation des liaisons C—H dans la chaîne latérale du polystyrolène.

La bande la plus appropriée pour déceler le greffage par le polystyrolène au faible taux de greffage est la bande à 700 cm^{-1}, puisqu'elle apparaît plus nettement que toutes les autres bandes (Déjà à 12,1% d'augmentation de poids, dans nos expériences.) Mais on ne peut pas apprécier le taux de greffage d'après l'intensité de cette bande, car la cellulose elle-même possède une forte absorption dans cette région. Si le taux de greffage est élevé, il est préférable de se servir dans ce but de la bande à 1550 cm^{-1}, à cause de l'absorption plus faible par la cellulose elle-même dans cette région.

D'après tous ces résultats on peut conclure que lors du greffage de la cellulose, les spectres infrarouges des produits obtenus présentent des bandes caractéristiques des monomères employés. On peut utiliser ces bandes non seulement pour identifier la nature chimique du monomère greffé, mais également pour déterminer le taux du greffage.

Propriétés de la Cellulose Greffée

Le greffage provoque une modification notable de certaines propriétés de la cellulose. L'étude des propriétés mécaniques des celluloses greffées révèle par contre que la résistance à la traction des fibres isolées n'est pas modifiée par le greffage. Il diminue évidemment son numéro métrique par suite de l'augmentation de son poids. Il s'en suit une légère diminution de la résistance spécifique des fibres (rapportée à 1 g de produit).

D'après les données reproduites dans le Tableau I, on voit que la cellulose greffée avec l'acrylonitrile ou le méthacrylamide est résistante aux micro-organismes, c'est à dire que la perte de la résistance mécanique après le pourrissement est moindre pour les produits greffés que pour la cellulose initiale.

La résistance à la chaleur des celluloses greffées par l'acrylonitrile ou par le méthacrylamide s'accroit avec l'augmentation du taux de greffage (voir Tableau I.)

La capacité tinctorielle de la cellulose peut être augmentée (*a*) vis à vis des colorants acides par greffage avec le nitrile acrylique et (*b*) vis à vis des colorants basiques par greffage avec l'acide methacrylique.

On voit d'après les Figures 2 et 3 que l'absorption de vapeurs d'eau par la cellulose diminue après le greffage avec le nitrile acrylique ou le styrolène; elle diminue d'autant plus que le taux de greffage est plus grand. Néanmoins, il faut remarquer que la chaleur de mouillabilité par l'eau, et la chaleur de sorption de vapeurs d'eau ne changent ni pour la cellulose elle-même ni pour la cellulose greffée si l'on augmente la dose d'irradiation de 5×10^5 à 1×10^6 r. D'après les données réunies dans les Tableaux I et II, on voit par contre, que le greffage avec l'acrylonitrile ou le styrolène diminue la chaleur de mouillabilité par l'eau, et ceci d'autant plus que le taux de greffage est plus élevé. On observe le même résultat après le greffage de la cellulose avec le methacrylate ou avec le methacrylate de méthyle. On peut expliquer cela par la nature moins hydrophile des chaînes des polymères par rapport à celle de la cellulose. D'autre part, le greffage à lieu principalement sur les parties amorphes, moins denses, de la fibre, ce qui a pour conséquence de provoquer un empêchement de la pénétration des molécules d'eau dans la fibre.

En résumé on peut dire que l'emploi de la méthode d'irradiation par les rayons γ permet de modifier largement les propriétés des matériaux cellulosiques. La méthode de greffage par irradiation présente un avantage par rapport à d'autres méthodes du fait qu'elle ne nécessite pas d'activation préalable de la cellulose et conduit à des produits greffés particulierement purs.

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Résumé

Dans ce travail on a étudié quelques propriétés des celluloses greffées avec le méthacrylate de méthyle, l'acrylate de méthyle, l'amide méthacrylique, le nitrile acrylique et le styrolène. Le greffage a été obtenu par irradiation avec des rayons gamma. Les spectres infrarouges contiennent des nouvelles bandes, caractéristiques des monomères greffés. Au moyen de ces bandes, on peut non seulement identifier le monomère greffé, mais également reconnaître le taux de greffage. Le greffage de la cellulose ne diminue pas sensiblement sa résistance á traction. Par contre, il augmente sa thermostabilité, sa résistance á l'action des microorganismes, son affinité pour les colorants et sa capacité

d'adhésion. La thermostabilité et la résistance á l'action des microorganismes des copolymères de cellulose, greffées par l'amide méthacrylique ou par le nitrile acrylique, augmentent avec le taux de greffage. Le greffage de la cellulose provoque une variation de sa chaleur de mouillage par l'eau et de sa capacité d'adsorption de vapeur d'eau. Cette variation peut être soit positive, soit négative selon la nature chimique des monomères greffés. Ainsi le greffage par irradiation avec des rayons gamma permet de modifier notablement les propriétés des matériaux cellulosiques.

Synopsis

Some properties of celluloses grafted with methyl methacrylate, methyl acrylate, methacrylic amide, acrylonitrile and styrene have been studied. Grafting was carried out by irradiation with gamma-rays. The infrared spectra contain new bands, characteristic of the grafted monomers. On the basis of these bands, it is possible to identify the grafted monomer and to determine the content of it. Grafting of cellulose decreases appreciably its resistance on traction. Contrarily, it increases its thermostability, its resistance to microorganisms, its dyability and adhesion capacity. The thermostability and resistance to microorganisms of cellulose copolymers, grafted with methacrylic amide or acrylonitrile, increase with the degree of grafting. Grafting of cellulose modifies its heat of melting with water as well as its water vapor absorption capacity. This variation can be either positive or negative depending the chemical nature of the grafted monomers. As conclusion, grafting by gamma-irradiation modifies considerably the properties of cellulose materials.

Zusammenfassung

In der vorliegenden Arbeit wurden einige Eigenschaften von mit Methylmethacrylat, Methylacrylat, Methacrylamid, Acrylnitril und Styrol aufgepfropfter Cellulose untersucht. Die Aufpfropfung wurde durch Bestrahlung mit γ-Strahlen erhalten. Die Infrarotspektren enthalten neue, für die aufgepfropften Monomeren charakteristische Banden. Mit Hilfe dieser Banden kann nicht nur das aufgepfropfte Monomere identifiziert werden, sondern man kann auch das Ausmass der Aufpfropfung erkennen. Die Aufpfropfung auf Cellulose vermindert deren Zugfestigkeit nicht merklich. Dagegen erhöht sie die thermische Beständigkeit, die Beständigkeit gegen die Einwirkung von Mikroorganismen, die Affinität für Farbstoffe und die Adhäsionsfähigkeit. Die Thermostabilität und die Beständigkeit gegen die Einwirkung von Mikroorganismen von Cellulosepfropfcopolymeren mit Methacrylamid oder Acrylnitril nimmt mit dem Pfropfungsgrad zu. Die Aufpfropfung auf Cellulose ruft eine Änderung ihrer Benetzungswärme mit Wasser und ihrer Absorptionskapazität für Wasserdampf hervor. Diese Änderung kann je nach der chemischen Natur des aufgepfropften Monomeren positiv oder negativ sein. Die Aufpfropfung mit Hilfe von γ-Strahlen erlaubt so eine beträchtliche Modifizierung der Eigenschaften von Cellulosematerialien.

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Graft Copolymers of Polyethylene and Acrylic Acid. II.

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INTRODUCTION

In recent years the formation of graft copolymers has received considerable attention. Much of this activity can be traced to speculation that unique properties can be built into a material by grafting techniques. Ionizing radiation has provided a convenient and clean method of activating a substrate polymer and undoubtedly has added impetus to this field of research. Of course, many other activating agents can be and have been used successfully. Among the prominent reagents used are ozone,[1] oxygen,[2] NO_2[3] and various peroxides.[4]

In a previous paper we described the properties obtained from the grafting of 8% acrylic acid to high density polyethylene.[5] In this paper we present further data on this same graft copolymer and also compare the properties of this material to companion products containing 5 and 20% acrylic acid.

Our reason for carrying out these studies was aimed at pursuing a concept of producing thermally sensitive crosslinks which could improve the properties of polyethylene. Acrylic acid was chosen because it was a potentially strong hydrogen bonder. It is obvious that increased chemical reactivity would also be introduced into the polyethylene with the grafting of acrylic acid.

PREPARATION OF COPOLYMERS

The graft copolymers described in this publication were all prepared by the method of Chapiro et al.[6] Further details of the preparation can be found in the publications of Rieke and co-workers.[5,7]

The polyethylene utilized was a commercially available high density material produced by the Dow Chemical Company, but which contained no additives. Polymers were activated by passing the dry material under the electron beam of a Van de Graaff accelerator operating at 2 m.e.v. and with a beam current of 220 μamp. Details are enumerated in Table I.

The activated polymers were dispersed in a solution of toluene and acrylic acid, the system was purged of air, the temperature was elevated to 120–

TABLE I
Reaction Conditions and Product Description

Measurement	Sample number		
	2478	102	2133
Radiation dose, Mrad	0.8	0.8	2.0
Radiation intensity, dose/pass	0.8	0.4	0.4
Reaction temperature, °C.	120–140	120–140	120–140
Melt index[11]			
Base polymer	3	3	3
Product	1.0	0.9 (2.1)[a]	0.3
Acrylic acid, %	5.2	8.2	20.3
Soluble material, %[b]	—	3.7	2.5

[a] Measured on extruded material.
[b] Solubility in 5:2 methanol:xylene, room temperature.

140°C., and the reaction was carried out for a predetermined period of time. At the end of the reaction the product was dispersed in water to free it of unreacted impurities, acrylic acid monomer, and polyacrylic acid. Dow-Badische technical grade acid was utilized in all experiments, and nitration grade toluene was utilized as the diluent.

The graft content was determined from infrared analysis of thin copolymer films. The hydroxyl (3.2 μ) and the carboxyl (5.8 μ) bands were compared to the polyethylene band at 13.86 μ. The per cent acid present in the polymer was then determined from equations developed from carefully calibrated samples of graft copolymers.

CRYSTALLINITY

Absolute crystallinity values were obtained by the method of Aggarwal and Tilley[13] and are reported in weight per cent crystallinity. Table II enumerates values obtained with extruded pellets, quenched moldings, and quenched moldings subsequently annealed at 100°C. for 2 hr. The crystallinity values obtained from the pellets are slightly high due to the presence of some orientation produced during the extrusion process.

TABLE II
Crystallinity Data for Quenched and Annealed Graft Copolymers

	Crystallinity, wt.-%			
	0% Acrylic acid	5.2% Acrylic acid	8.2% Acrylic acid	20.3% Acrylic acid
Pellets	83.7	85.0	77.5	81.8
	83.0[a]	—	77.6[a]	—
Quenched	70.5	78.2	76.9	77.7
Annealed[b]	74.8	75.8	67.8	70.6

[a] Data previously reported.[5]
[b] Annealed 2 hr. at 100°C.

Crystallinities observed on the quenched graft copolymer samples are about 7–8% higher than observed on the control. The increase is virtually independent of the acrylic acid content of the copolymers. This difference may be due to the acrylic acid functionality promoting crystallization in the polyethylene. Some data[14] have indicated that the addition of small amounts of graft copolymer in high density polyethylene may promote crystallization under certain conditions.

While annealing increases the crystallinity of polyethylene, as expected, the crystallinity of the graft copolymers decreases. The annealing temperature, 100°C., is sufficiently high that the polyacrylic acid branches should have considerable mobility within the polyethylene matrix which probably disrupts the regrowth of crystallites in the polyethylene.

MECHANICAL PROPERTIES

Various mechanical properties have been measured over the temperature interval −30 to +120°C. and compared to the previously reported properties measured on the base polyethylene and the 8.2% graft copolymer.[5] Tests were conducted as close as possible to the published A.S.T.M. test methods.[8–10] Specimens were injection-molded into standard test specimen bars with a reduced section 2.5 in. long, 0.5 in. wide, and 0.125 in. thick. Crosshead travel speed for the tensile tests was 0.2 in./min. Each point on the curves is an average of five separate determinations. Dynamic modulus measurements were made with a torsion pendulum apparatus

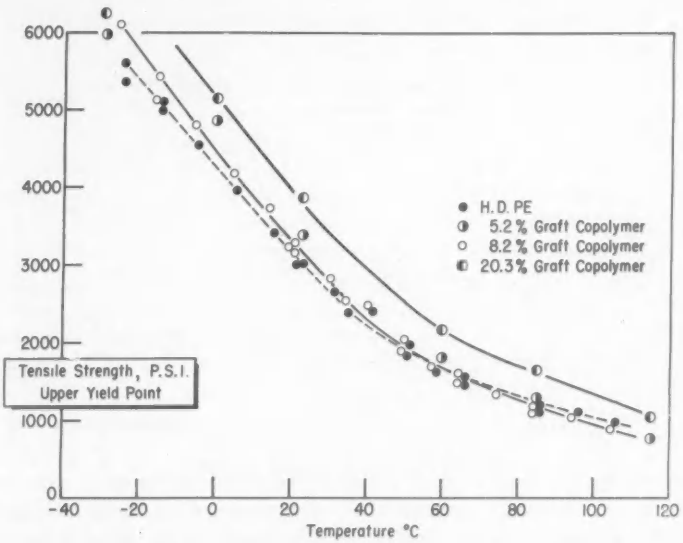

Fig. 1. Tensile strength at upper yield point vs. temperature.

purchased from Askania-Werke A.G., Berlin-Friedenau, Germany. The frequency range varied from 0.2 to 2.0 cycles/sec.

Tensile Strength

Variation of the tensile strength, at the upper yield point, as a function of temperature is illustrated in Figure 1. The three graft copolymers and polyethylene are shown. The base polyethylene and the 5 and 8% acrylic acid graft copolymers exhibit nearly identical tensile strengths over the entire temperature interval. At the lowest temperatures studied the graft copolymers appear to exhibit an improvement of approximately 500 psi, which decreases with increasing temperature until the curves converge at about 55 °C. The 20% acrylic acid graft copolymer follows the same trend observed with the other materials but is always about 500–1000 psi higher than polyethylene over the entire temperature interval. This higher strength may be due to a slight amount of crosslinking occurring in the graft copolymer during fabrication through anhydride formation. In general the behavior of the four materials is nearly identical.

Per Cent Elongation

Examination of elongation data, also at the upper yield point, shows that the test results are much more reproducible and follow predicted trends over the temperature interval −30 to +50°C. (Fig. 2). Above 50°C.

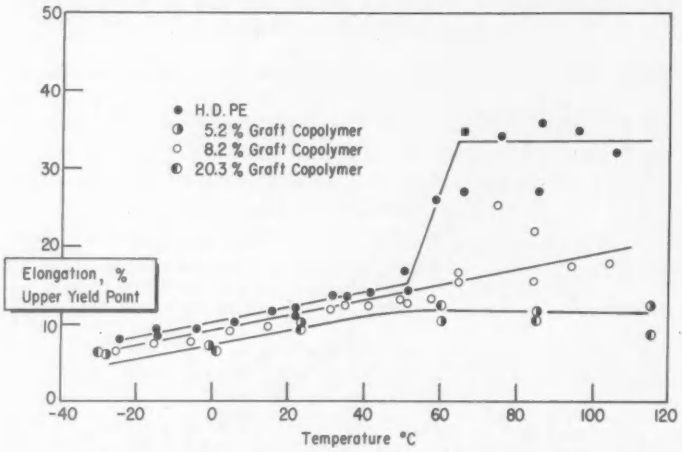

Fig. 2. Per cent elongation at upper yield point vs. temperature.

considerable data scatter is observed particularly in the graft copolymer specimens. Visual examination of specimens while being elongated provides a ready answer. Samples tested above 50°C. show evidence of nonuniformity and they elongate in localized regions rather than uniformly

across the specimen area. Specimens with the highest graft level show the effect in a more pronounced manner and tend to show the most heterogeneous breaks.

Tensile Modulus

Figure 3 illustrates the initial modulus in tension for the materials under study. Although the initial slope of the stress–strain curve is most difficult to determine accurately, the curves constructed from the data

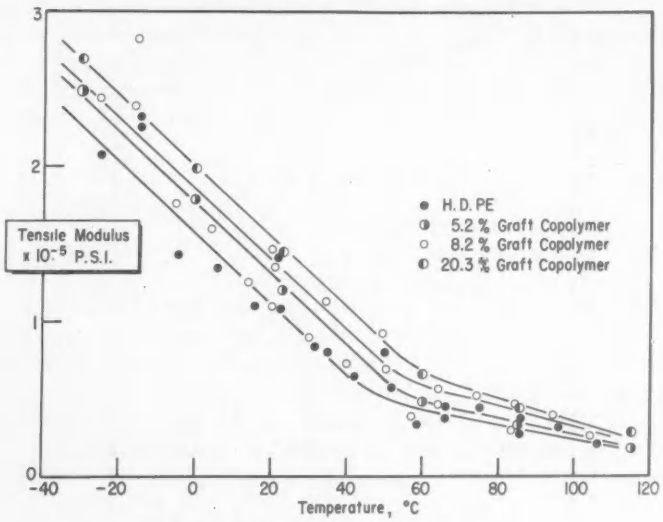

Fig. 3. Tensile modulus vs. temperature.

demonstrate a reasonable degree of consistency over the entire temperature interval. The moduli of the 5, 8, and 20% graft copolymers decrease linearly over the temperature interval −30 to +60°C. Similar behavior is noted for the base polyethylene, except that the break in the curve occurs at a slightly lower temperature of around 52°C. Above 60°C. the differences in moduli become increasingly less with increasing temperature and the lines tend to converge at approximately 125–130°C. which is close to the observed crystalline melting point of the base polyethylene.

Below the transition point, observed at 60°C., the change in modulus is approximately proportional to the weight per cent acrylic acid present in the graft copolymer.

Shear Modulus and Damping

A torsion pendulum instrument has been utilized to further characterize the copolymers. Measurements taken permit a computation of the complex shear modulus G^*. The real part G' is calculated from the oscil-

lation period, and G'' the imaginary part is calculated from the damping of the amplitude. The log decrement δ is given approximately by $(\pi G''/G') = \delta$. G' and δ are shown in Figure 4 for the three graft copolymers.

The curves are very similar to those obtained for the base high density polyethylene.[5] The characteristic transition for polyethylene is present at approximately -110°C., a small broad peak in the -25 to -50°C. region becomes more obvious with increasing acid content and has been related to the carboxyl group,[5] a transition about $+10$° is observed, and a

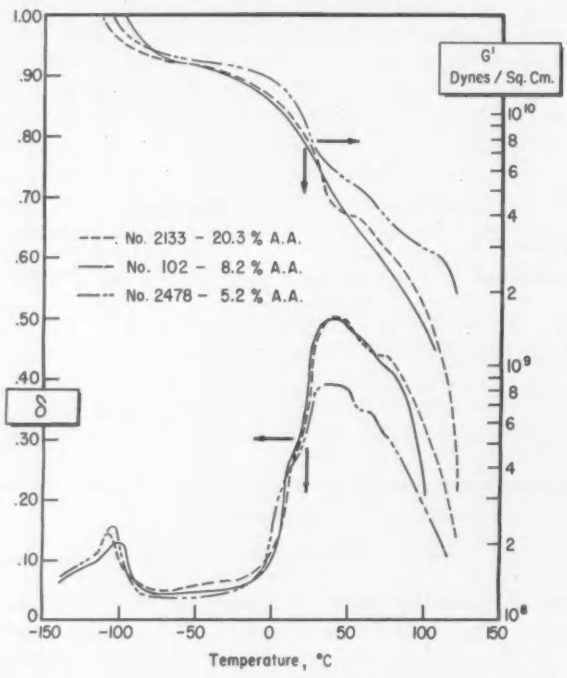

Fig. 4. Log decrement vs. temperature and shear modulus vs. temperature.

broad maximum with some fine structure is observed around 50°C. The overlap of the loss peaks related to the glass transition of polyacrylic acid and the crystalline polyethylene make it difficult to further separate the respective contributions.

Perhaps the most interesting aspect of the modulus curves is that the 5% graft copolymer exhibits a slightly higher modulus than either the 8 or 20% graft copolymers. This inversion would not necessarily be expected from the tensile moduli measured in static tests. However, our experiments have shown that small changes in crystallinity could account for the observed differences. For example, moduli measured on various polyethylenes show about a ten-fold change with crystallinity changes of 20–

30% while pure polyacrylic acid has a modulus only 2–3 times higher than observed on the base polyethylene. At the present time, we attribute this inversion to a small loss in crystallinity caused by the addition of 20% acrylic acid. Other observations made on systems of this type have shown this same inversion at higher graft levels.[12]

RHEOLOGICAL PROPERTIES

The flow and deformation characteristics of the polyethylene–acrylic acid graft copolymer are of considerable practical significance. Melt viscosities at processing temperatures and at high shear stresses are among the major factors influencing fabrication of the graft copolymers. At lower temperatures and at low shear stresses information on deformation helps define applications and uses.

Melt Viscosity

The melt flow properties were measured with an Instron capillary viscometer at temperatures of 175–250°C., and also with a rotational type rheometer over the same temperature interval. Since the results were the same, only the Instron data are reported here. Figure 5 illustrates representative flow curves for the 8.2% acrylic acid graft copolymer and the base polyethylene at a temperature of 225°C. The curves were constructed from the measured shearing stress at various shearing rates. Figure 5 readily demonstrates that while the graft copolymer has a slightly higher apparent melt viscosity, the flow curve is very similar to that obtained with the base polymer. The higher viscosity of the graft co-

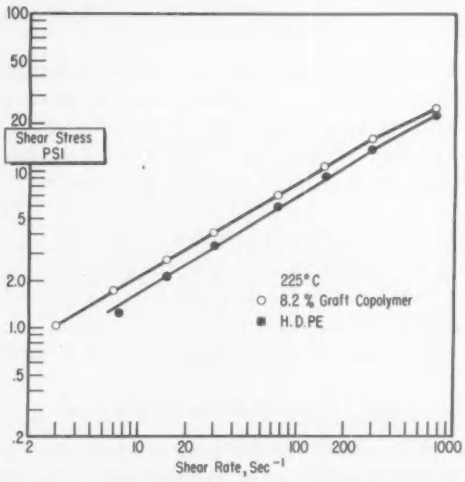

Fig. 5. Rheological flow curve, shear stress vs. shear rate.

polymer could be caused by a small amount of crosslinking caused by the irradiation or be due to interactions of the polyacrylic acid branches.

From a series of flow curves measured at various temperatures and similar to Figure 5, the apparent viscosity at a constant shearing stress of 3×10^5 dynes/cm.^{2} was calculated and plotted versus $1/T$. The plot is illustrated in Figure 6. The temperature dependence of melt viscosity for the

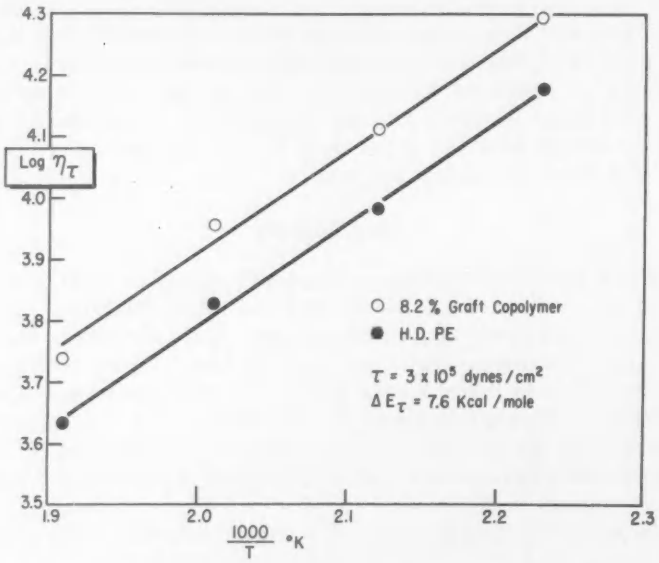

Fig. 6. Temperature dependence of melt viscosity at constant shear stress.

graft copolymer is the same as observed with high density polyethylene. Since the apparent activation energy at fixed shearing stress has been shown to be approximately independent of shearing stress,[15] an activation energy for viscous flow, ΔE_τ can be calculated. The value found for both polymers is 7.6 kcal./mole. This value is in agreement with other published values obtained on high density polyethylene.[15–17] These activation energies indicate that the grafted polyacrylic acid branches are either too few in number or are ineffective in altering the activation energy for viscous flow. Previous data have shown that polyethylene branches increase the activation energy[15,16] and we suspect the limited number of polyacrylic acid branches explains the lack of effect observed with the graft copolymers.

Thermal Deformation

The thermal deformation of the graft copolymers has been studied under 66 psi tensile stress using a method similar to that described in A.S.T.M. test method D1637-59T.[18] Results are illustrated in Figure 7

for the three graft copolymers and polyethylene. Small differences in expansion occur between 50 and 110°C. with the 20% copolymer showing the least expansion and the 5% material the most. The 8% graft copolymer and the polyethylene follow the same expansion curve. Above 115°C. the curves show nearly identical behavior. Back extrapolation of the steep portion of the curves yields a heat distortion temperature of approximately 115–117°C. for these materials. Cooling curves for the samples are also shown on Figure 7. Upon cooling we find that the polyethylene shows the greatest recovery and the 20% graft copolymer the

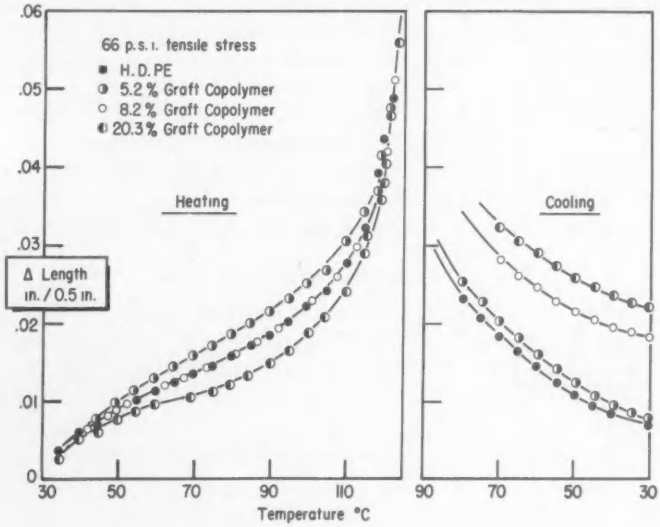

Fig. 7. Thermal deformation vs. temperature at 66 psi tensile stress.

least. The permanent set of the polyethylene is about 1.5% and that of the 20% graft copolymer about 5%. Some of this permanent elongation is undoubtedly caused by annealing and loss of crystallinity in the graft copolymer samples and some is due to a small amount of creep. Preliminary evidence indicates that the 20% graft copolymer has a greater tendency to creep at temperatures above 100°C. than do polyethylene and the graft copolymers containing lesser amounts of acrylic acid.

ADHESION

The introduction of adhesive qualities into polyethylene by the addition of carboxylic acid groups is one of the more important changes observed. Both peel adhesion and lap shear adhesion tests have been carried out and compared to polyethylene.

Peel

Peel adhesion values are extremely sensitive to a number of variables which include the bulk properties of the adhesive, the angle of peel, thickness, speed of test, and the adherent. Reported results were carried out by A.S.T.M. test methods[19] except with a pulling speed of 4 in./min. Details of the sample preparation can be found elsewhere.[5]

Figure 8 illustrates peel adhesion results for the 5, 8, and 20% copolymers when bonded to 0.002 in. soft aluminum and when the metal is peeled

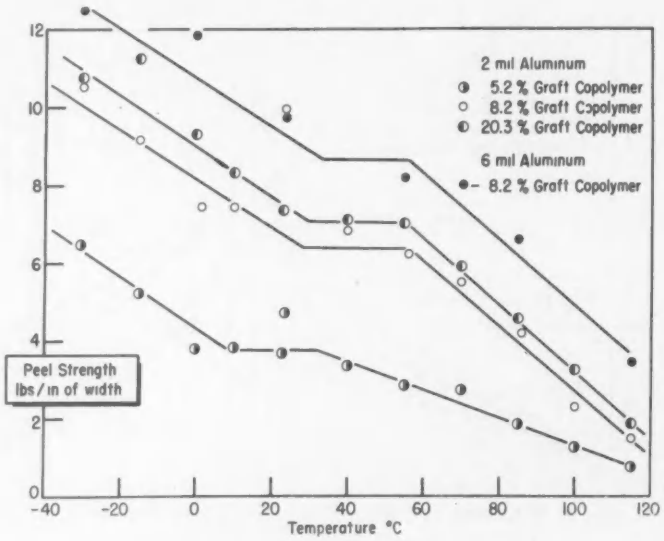

Fig. 8. 180° Peel adhesion vs. temperature.

from the copolymer. Results with 0.006 in. aluminum bonded to the 8% copolymer are also shown. The increased thickness of metal yields values about 1.5–2.0 lb./in. higher than obtained with the 2-mil metal.

The 5% copolymer exhibits considerably less resistance to peel than the 8 or 20% acrylic acid graft copolymers, but the 20% graft is only slightly superior to the 8% graft. The same relative relationship between the 8 and 20% grafts exists over the entire temperature range investigated. The adhesion decreases linearly with temperatures from −30 to +25°C., is almost independent of temperature from +25 to +60°C., and again decreases linearly above 60°C. but at a greater rate.

The 5% material shows about the same behavior in the low temperature region, however the plateau is shifted about 30°C. toward lower temperatures. At the high temperature end of the curve the adhesion again decreases linearly but at much slower rate than observed with the

other materials. The high density polyethylene exhibits almost no adhesion under these conditions of test.

The linear decrease in adhesion with increasing temperature observed in the temperature interval −30 to + 25°C. can be explained either by postulating an increase in the interfacial bond strength with decreasing temperature or by a change in the bulk properties of the polymer (providing the bond strength is sufficiently high that failure is in the polymer and not in the interface and also if the applied stress concentrated in the polymer is sufficient to cause failure). If the bulk properties were the only factor we would expect the adhesion to decrease at about the same rate as the bulk properties decrease. This is not observed. At the lower temperatures the change in adhesion is less than the change in either the tensile strength or the modulus, at the highest temperatures the adhesion changes at a greater rate. Since the bond strength undoubtedly increases with decreasing temperature linear curves would probably be expected for the temperature interval investigated. However, if both the bulk properties and the interfacial bond strength determine the observed peel strength then we can account for the shape of the various adhesion curves and also the shift of the plateau towards lower temperatures with the 5% graft copolymer.

Lap Shear Adhesion

The shear specimens were all prepared by bonding two 4 × 6 in. aluminum sheets together with an overlap of 0.50 ± 0.05 in. The aluminum sheet was type 2024-T3, 0.063 in. thick. The bonding was carried out in a specially designed jig to maintain uniform adhesive thickness and uniform overlap. Specimens were bonded in a platen press at a temperature of 200°C. with 2000 lb. platen pressure for 2 min. Specimens were cooled in the press. Specimens were sawed into 1 in. wide strips, the edges were discarded, and the remaining samples were conditioned at 23 ± 1°C., 50% R.H., for 7–9 days. Results are reported in pounds per square inch of lap.[20]

Figure 9 illustrates the experimental results. The best representation of the data indicates that the adhesion decreases linearly with increasing temperature. The rate of decrease is similar for all three graft copolymers. The 20% graft exhibits slightly less adhesion than does the 8% graft copolymer. The data obtained for the 5% copolymer shows considerably more variation than observed with the other two systems. This variation is most pronounced at the lowest temperatures where our instrument is operating very near maximum capacity.

Figure 9 readily demonstrates the differences between the graft copolymers and polyethylene. The polyethylene shows no measurable adhesion in the lap shear studies, and under most conditions samples delaminated during the preparation of the test specimens. The lap shear test provides a mechanism of eliminating, to some extent, the high localized stress concentrations found in peel tests. We therefore expect that the adhesion measured is much more a function of the interfacial bond strength and

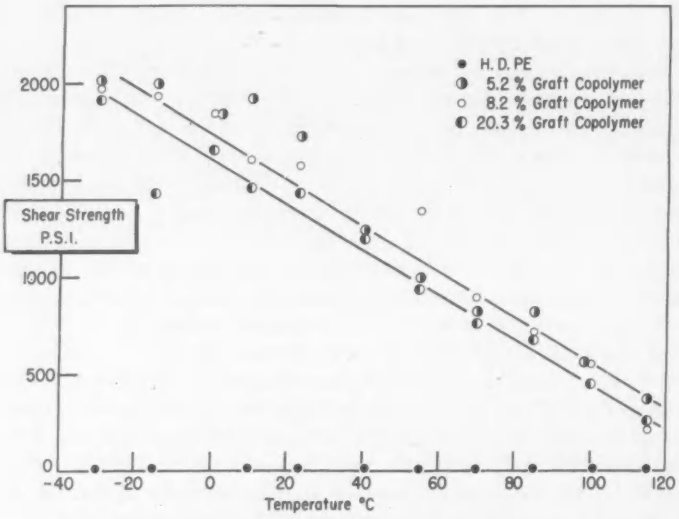

Fig. 9. Lap shear adhesion vs. temperature.

much less dependent on the bulk properties of the polymers utilized. On this basis the shear strengths observed are consistent with the observed peel data. At the present time we have no measure of the theoretically possible bond strength attainable with these systems, since many of the breaks start at a surface irregularity. However, observations made on samples indicate that the breaks are largely interfacial in character.

DISCUSSION

The properties of 5.2, 8.2, and 20.3% polyethylene–acrylic acid graft copolymers have been measured. In most cases the mechanical properties follow trends observed with the polyethylene substrate. However, certain differences are observed. Crystallinity measurements indicate that the graft copolymer introduces secondary effects upon the polyethylene crystallinity. These effects are essentially those of nucleation when a sample is quenched from the melt, and inhibition of crystallite regrowth when samples are annealed above the glass transition temperature of polyacrylic acid. Low graft frequencies and relatively long polyacrylic acid side chains best explain this behavior.

Mechanical properties (Figures 1–3) are substantially similar to properties of high density polyethylene. Tensile strength and elongation closely follow the pattern characteristic of the backbone polymer. Above 60°C. the elongation of the graft copolymer becomes non-uniform which is indicative of localized imperfections in the continuous phase. The increase in elongation observed in the polyethylene has been explained by

an increasingly mobile polyethylene structure.[5] This effect is offset by the acrylic acid imperfections in the graft copolymers.

Tensile moduli (Fig. 3) follow the characteristic pattern observed when a rigid filler is added to a flexible polymer. Polyacrylic acid would behave much like a rigid filler while in the glass state and the moduli increase with increasing acid content. Above 60°C. the effect is much less pronounced, and convergence occurs around 125–130°C.

Dynamic property data have led to further validation of our conclusions. Both the log decrement and the shear modulus closely approximate polyethylene. The increased peak at +10°C. suggests that there may be slightly more branching in the graft copolymer, but only to a very limited degree. Unfortunately, the broad polyethylene loss peak at 50°C. overlaps the loss peak for the glass transition of polyacrylic acid to such an extent that further interpretation is difficult. The small increase in modulus measured with the 5% copolymer, when compared with the 8 and 20% copolymers, demonstrates the importance of disruptions in the polyethylene crystal lattice. These data correlate well with the observations reported in Table II. Under comparable conditions of crystallinity the graft copolymers tend to exhibit slightly higher moduli than do unmodified polyethylene.

Melt viscosity and thermal deformation again demonstrate the similarity between the various systems. The slightly higher viscosity observed with the 8% graft copolymer is probably indicative of a slightly higher molecular weight polymer. This increased molecular weight could be caused by either crosslinking or by the polyacrylic acid branches. The latter explanation is the more likely. The ΔE_τ of 7.6 kcal. obtained for both polyethylene and the 8% graft copolymer indicates equivalent flow behavior, and further indicates very few branches are present in the graft copolymer.

Further efforts have been made to characterize the frequency of grafting.[21] Polyacrylic acid homopolymer produced during the graft polymerization reaction was analyzed by the method of Kagawa and Fuoss.[22] The molecular weight of the homopolymer was 7200 based on a D.P. of 100. Assuming that the grafted acrylic acid has the same molecular weight as homopolymer and that 7200 is a number-average molecular weight, the frequency can be readily calculated if we know the molecular weight of the substrate. For the particular polyethylene we utilized $\bar{M}_n$ is 50,000, and the calculated frequency is about 0.7 branches/polyethylene molecule. A calculation based upon the number of active sites produced, although less exact, indicates that the maximum number of grafting sites is less than 3/molecule. Apparently most of the active sites are utilized for grafting.

The greatest observable change is in the adherability of the graft copolymer. The peel adhesion at room temperature is about 8 lb./in. while that of the polyethylene is less than 1 lb./in. Lap shear adhesions are about 1400 psi versus nil for the polyethylene. The observed peel adhesion results have been explained in terms of an interplay of the interfacial bond energy and the bulk properties of the polymer. Visual ob-

servations indicate that bond rupture is the predominant effect at low temperatures.

The lap shear results indicate predominant interfacial bond rupture. Most breaks appear to start at a surface irregularity, which probably explains the lack of spread observed in the lap shear adhesions measured on copolymers of differing acid levels.

CONCLUSIONS

While we have not succeeded, at least to the degree that we might have hoped, in obtaining a structure which could produce many thermally sensitive crosslinks, a number of interesting observations have been made on polyethylene-acrylic acid graft copolymers containing about one branch per molecule. We have demonstrated how, even with this limited number of branches, the physical and mechanical properties of polyethylene can be altered.

The grafting technique has permitted us to build adhesive characteristics into polyethylene without destroying other desirable properties. It has also permitted us to put a polar and nonpolar polymer pair together to obtain a resultant compatible copolymer. Attempts to accomplish this result by various blending techniques have not been successful.

We believe that this work readily demonstrates the properties which need to be studied and the conditions necessary to prepare graft copolymers with unusual properties.

We would like to express our appreciation to J. W. Sembower who made most of the viscosity measurements, J. E. Burkholder who determined the mechanical properties and the adhesion characteristics, and S. G. Turley who measured the dynamic properties and assisted in the interpretation.

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Synopsis

Graft copolymers of high density polyethylene and acrylic acid have been prepared by preirradiation activation of the polyethylene. The properties of a 5.2, 8.2, and 20.3% graft copolymer have been compared. Measurements include crystallinities, mechanical and dynamic properties, melt flow and thermal deformation, and peel and lap shear adhesions. Most properties correspond closely to what is expected from a graft copolymer containing about one branch per molecule, and closely parallel the properties of the backbone polymer. The adhesion of the graft copolymer is much greater than observed with unmodified polyethylene.

Résumé

On a préparé des copolymères greffés de polyéthylène de haute densité et d'acide acrylique. On compare les propriétés des copolymères greffés à 5.2, 8.2 et 20.5%. Les mesures portent sur les cristallinités, les propriétés mécaniques et dynamiques, l'écoulement à l'état fondu et al déformation thermique, l'écaillement et l'adhésion lors de la traction d'une pellicule. La plupart des propriétés correspondent de près à ce qu'on attend d'un copolymère greffé contenant environ une ramification par molécule, et sont parallèles aux propriétés du polymère qui forme la chaine principale. L'adhésion du copolymère greffé est bien plus grande que celle observée avec du polyéthylène non-modifié.

Zusammenfassung

Pfropfcopolymere aus Polyäthylen hoher Dichte und Acrylsäure wurden durch Vorbestrahlung des Polyäthylens dargestellt. Die Eigenschaften von Copolymeren mit 5,2, 8,2, und 20,3% Aufpfropfung wurden verglichen. Gemessen wurden die Kristallinität, mechanische und dynamische Eigenschaften, Fliessen der Schmelze und thermische Deformation sowie Adhäsion, Ablösungs- und Uberlappungsscherbeanspruchung. Die meisten Eigenschaften entsprechen ziemlich genau dem, was man von einem Pfropfcopolymeren mit etwa einer Verzweigung pro Molekül erwarten würde und ähneln sehr den Eigenschaften des Ausgangspolymeren. Die Adhäsion des Pfropfcopolymeren ist viel grösser als die des nicht modifizierten Polymeren.

Discussion

L. Valentine (*Teddington, Middlesex, Great Britain*): Has Dr. Rieke made any observations on the effects of high humidity on adhesion, and in particular the effect of cycling the sample through high humidity and then remeasuring adhesion at low humidity again?

J. K. Rieke: Some qualitative observations indicate that humidity can affect the strength of the adhesive bond. However, the magnitude of the effect depends upon both the substrate and the quality of the initial bond. The better the initial bond

(providing no substrate corrosion) the more resistance exhibited against transient effects of high humidity.

L. S. Rayner (*I.C.I. Ltd., Herts, Great Britain*): Dr. Rieke referred to nucleation by the acrylic acid component. Did this have any effect on the spherulite size?

J. K. Rieke: Yes. Initially the acrylic acid component tends to produce many small spherulites. Upon annealing the long acid side-chains tend to interfere with regrowth of crystallites and probably with larger spherulites as well.

S. H. Pinner (*B.X. Plastics Ltd., Essex, Great Britain*): What effect does residual homopolyacrylic acid have on the adhesion to aluminum?

J. K. Rieke: The graft copolymer, prepared and reported, may have a varying number of acrylic acid chains per polyethylene molecule. We cannot guarantee that there is no polyacrylic acid homopolymer present in the materials studied, but what is present is compatible in our system. When larger amounts of polyacrylic acid are present incompatibility arises and the product tends to be moisture sensitive in these areas while adhesion tends to become non-uniformed and spotty.

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Dynamic Mechanical Properties of Some Graft Copolymers

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INTRODUCTION

In the last few years a large amount of experimental work has been carried out in the field of the applications of dynamic mechanical methods to the investigation of high polymers. As a result of improvements of the electronic techniques, the sensitivity and accuracy of these methods have been increased more and more, so, at present, they can be regarded as a very valuable tool for the investigation of structure of polymeric materials and of mobility of molecular chains.

Recently, a large number of high polymers and copolymers of different types have been investigated by dynamic mechanical methods with very interesting results, but not much work has been made in the field of graft copolymers. This problem appears to be worthy of investigation and interesting features of graft copolymerization might come out from accurate measurements of dynamic mechanical properties.

In the present work samples of different graft copolymers have been examined by an electrostatic resonance method at frequencies of the order of several kilocycles, and the experimental results compared with those for the corresponding homopolymers and their mixtures.

EXPERIMENTAL

The method employed is based on the same principle as one used by us previously,[1] but it has been noticeably improved in order to increase its sensitivity and exclude causes of additional losses.[2,3] Moreover circular plates were used instead of cylindrical rods, and there was no dielectric material between electrode and vibrating plate.

The samples used were in the form of circular plates (3 mm. thick, 36 mm. diameter), vibrating on their lowest flexural symmetrical modes, with nodal circles and no nodal diameter. The vibromotive force was supplied by the electrostatic attraction between the specimen (which is metallized) and a small circular electrode, kept parallel to the vibrating

surface and very near to it. The same electrode was used for exciting vibrations, and also for measuring the vibration amplitude.

The use of circular plates has some advantages over samples of different shapes. In first place, a larger amplitude of vibration can be obtained for a given vibromotive force and a given frequency.[4] Moreover it is quite easy to support a small plate, without perturbing its vibrations, by simply laying it on three pins, located in small holes on a nodal circle. In our device, two of the supporting pins are made of copper and Costantan and function as thermocouples for measuring the temperature of the sample. These two broken thermocouples, which are connected through the metallized surface of the sample, allow measurement of the temperature of the sample by the use of a potentiometer with an accuracy of $\pm 0.2°$K., independent of the rate of temperature variation and the nature of the metallic coating.[4]

An additional advantage of this device is that the electrode is not fixed; it can be moved by an external micrometer screw, so its positions can be properly adjusted at any time in the course of the measurements to compensate for deformations of the support caused by changes of temperature or accidental shocks.

The whole support, electrode, and vibrating plate assembly is enclosed in a metallic vacuum container which can be inserted in a Dewar flask (for measurements at low temperatures) or in a thermostat (for measurements at high temperatures). During the measurements of resonant frequency and damping factor, the pressure in the container is kept at about 10^{-3} mm. Hg, in order both to reduce additional energy dissipation due to the air viscosity and to avoid temperature variations during the time in which those properties are determined. During the warming or the cooling stages, an exchange gas (dry nitrogen or helium) is introduced in the container at a pressure of about 1 mm. Hg, in order to facilitate heat exchanges.

Measurements can be carried out between the melting or softening point of the material examined and liquid nitrogen temperature. Temperatures below the boiling point of nitrogen may also be reached by filling the Dewar flask with liquid nitrogen and pumping it by means of a high speed rotatory pump.

The resonant frequency is measured by means of a quartz-controlled electronic counter (Hewlett-Packard, type 521 CR). The accuracy of the measurements generally depends on the sharpness of the mechanical resonance of the specimen, being no better than the larger of the following values: several units $\times 10^{-1} \times Q^{-1}$ or several units $\times 10^{-5}$. The damping factor Q^{-1} is measured from the width of the resonance curve. In this case, the accuracy is limited by the measurement of the maximum amplitude at the resonance and of the two side measurements of $1\sqrt{2}$ of the maximum amplitude. The average error affecting Q^{-1} is of the order of 10^{-2} of its value.

From the resonant frequency f corresponding to the first flexural vibra-

tion modes of a free plate with m nodal circles and n nodal diameters and radius r, the sound velocity v can be calculated by means of eq. (1):

$$f_{m,n} = \alpha_{m,n}(h/r^2)v \tag{1}$$

where for $m = 1$, $n = 0$, $\alpha = 0.4170$.

From the sound velocity v, the density d, and the Poisson's coefficient σ the elastic modulus E can be calculated by eq. (2):

$$v = [E/d(1 - \sigma^2)]^{1/2} \tag{2}$$

Polystyrene–Polybutene System

In Figure 1 the sound velocity and the damping factor determined in mixtures of polystyrene and atactic polybutene-1 obtained by mixing the two components in the molten state are reported as functions of temperature. The v–T curves for all the examined samples exhibit three successive increases of slope at T_γ (−130°C.), T_β (−35°C.), and T_g (+80°C.)

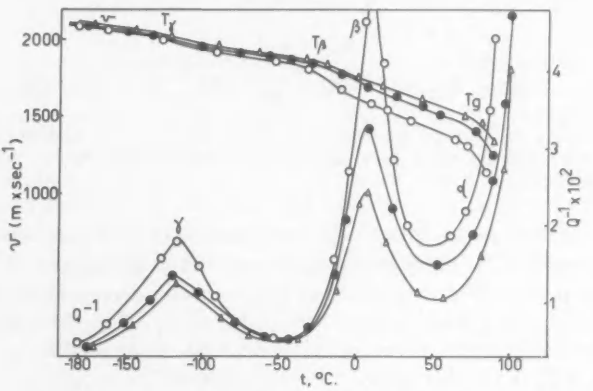

Fig. 1. Sound velocity and damping factor in polystyrene–atactic polybutene mixtures of varying polybutene contents: (○) 22%; (●) 12%; (△) 7% polybutene.

The damping factor versus temperature curves show three relaxation phenomena; of these, the first two (γ and β) are characterized by a maximum of mechanical losses at −118 and +8°C., respectively; the third (α) is characterized by a rapid increase of the damping factor at temperatures in neighborhood of T_g.

Figure 1 shows that on changing the ratio of the two components (polystyrene and polybutene) in the mixtures, the positions of the various singular points both in the v–T and in the Q^{-1}–T curves remain practically unchanged; at the same time, with increasing polybutene content, the changes of slope of v–T curves at T_γ and T_β become more marked, the heights of γ and β damping maxima become higher, and the values of the thermal coefficient of the sound velocity dv/dT, at temperatures between

room temperature and T_g, increase. A small shift of T_g toward lower temperatures with increasing butene content is also observed.

Qualitatively similar behavior is shown by the curves reported in Figure 2, in which the sound velocity and the damping factor are reported as functions of temperature for some samples of polystyrene grafted on peroxidated atactic polybutene-1. A comparison of these curves with those cor-

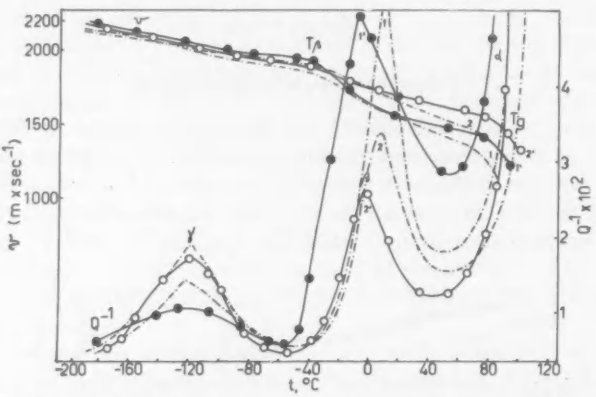

Fig. 2. Sound velocity and damping factor in polystyrene (——) grafted on peroxidated atactic polybutene and (–·–) in the corresponding mixtures; (●) 22% polybutene; (○) 12% polybutene.

responding to mixtures of the same compositions (dotted lines) shows that while the position of the γ peak remains practically unchanged, the β peak is shifted toward lower temperatures and its height decreased by grafting; moreover, in the grafted samples, the value of dv/dT in the temperature range from room temperature to T_g is lower than in the mixtures, while the position of T_g is a little higher.

Styrene–Acrylonitrile/Butadiene–Acrylonitrile System

In Figure 3, the sound velocity and the damping factor are reported against temperatures for some mixtures of a 80/20 styrene–acrylonitrile copolymer (SN) with a 80/20 and a 60/40 butadiene–acrylonitrile copolymer (BN), obtained by mixing the corresponding melts in different ratios.

The sound velocity versus temperature curves of these materials exhibit two successive increases of slope at T_g' (-56 and -28°C. for mixtures containing 80/20 and 60/40 BN, respectively) and at T_g($\sim +86$°C. for all samples); correspondingly, the damping factor versus temperature curves show two regions of high dissipation, one at lower temperature with a maximum at T'_d about -27°C. and $+5$°C. for mixtures containing 80/20 and 60/40 BN, respectively, and another, starting at temperatures just above T_g, characterized by a rapid increase of mechanical losses with increasing temperature.

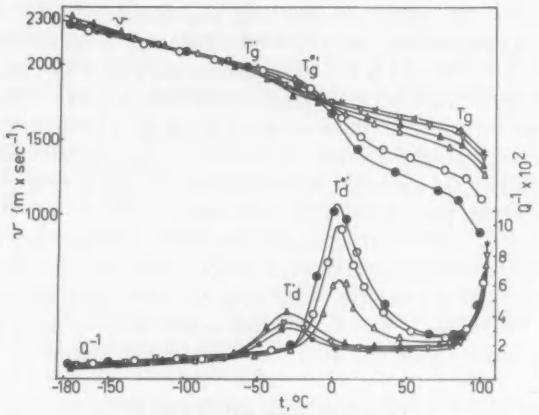

Fig. 3. Sound velocity and damping factor in mixtures of Buna N with polystyrene–acrylonitrile copolymers: (●) 20% BN 60/40; (○) 18% BN 60/40; (△) 12% BN 60/40; (▲) 10% BN 80/20; (▽) 8% BN 80/20; (*) 6% BN 80/20.

By increasing the BN/SN ratio, keeping the composition of each component in the mixture constant, the change of slope at T'_g becomes more marked, the height of the damping maximum at T'_d becomes higher, and the value of dv/dT at temperatures between room temperature and T_g increases. The positions of all single points in both v–T and Q^{-1}–T curves remain practically unchanged. On the other hand, on varying the composition of the butadiene–acrylonitrile copolymer (increasing its butadiene content), a shift of both T'_g and of the damping maximum is observed towards lower temperatures.

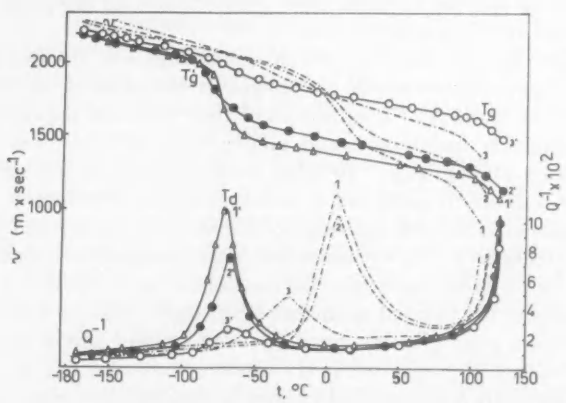

Fig. 4. Sound velocity and damping factor in (——) BN/SN grafted copolymers and (– – –) in the corresponding mixtures: (△) 20% BN 60/40; (●) 18% BN 60/40; (○) 10% BN 80/20.

In Figure 4, the sound velocity and the damping factor are reported against temperatures for a sample of 80/20 styrene–acrylonitrile copolymer grafted on a 80/20 and a 60/40 butadiene–acrylonitrile copolymer with different weight ratios between grafted and base polymer. The shapes of these curves are similar to those reported in Figure 3, but, on comparing the results for the grafted materials with those for the corresponding mixtures characterized by the same SN/BN ratios and the same compositions of the two components, these main differences can be noticed: (*1*) the transition temperature T_g' and the maximum damping temperature are both shifted towards much lower temperature for the grafted materials; (*2*) these shifts are more marked in materials containing BN with higher acrylonitrile content; (*3*) the values of dv/dT at temperatures between room temperature and T_g are higher for the mixtures than for grafted materials.

DISCUSSION OF RESULTS

The diagrams of the dynamic mechanical properties of the polystyrene–polybutene mixtures as a function of temperature can be considered as superpositions of the corresponding diagrams for the two individual homopolymers.[6,7]

The points T_γ, T_β, and T_g, which appear in the v–T curves and the associated relaxation phenomena γ, β, and α are related with motions of C_2H_5 of polybutene branches, with main-chain motions of polybutene, and with main-chain motions of polystyrene, respectively. The positions of the transition temperatures T_γ and T_β and those of the corresponding damping maxima in the mixtures are coincident with the corresponding points relative to the pure atactic polybutene-1.[5] However, the transitions at T_g, which marks the initial softening of polystyrene chains in the mixture is shifted a few degrees towards lower temperatures as compared with the glass transition of pure polystyrene.

The fact that the same transitions, characteristic of the two individual homopolymers, appear nearly unchanged in the plots of the mechanical properties as function of temperature of their mixtures indicates that the two components (polybutene and polystyrene) have not lost their own individuality after mixing. In other words, during the mixing, a certain tendency is shown by molecules of each type to be surrounded by molecules of the same kind to form aggregates, which are characterized by the same chain mobility as in the corresponding pure homopolymer, being so little affected by the presence of the other component in the mixture. However, the increase of the thermal coefficient of the sound velocity and the shift of the transition point of polystyrene T_g towards lower temperatures, caused by the presence of polybutene in the mixture, indicates that, at least in the high temperature range, a certain degree of compatibility exists between the two components and that polybutene, at temperatures above its softening point, acts as a polymeric plasticizer.[6] This effect, however, is not marked.

The relation of this to the main differences existing between the dynamic

mechanical behaviors of the polystyrene–polybutene mixtures and those of the grafted materials of the same compositions, namely the decrease of height of the damping maximum β and the shift of the corresponding temperature towards lower values, can be attributed to the structural changes induced by grafting. In the grafted materials, new structures are formed which are characterized by a high degree of branching; in these structures, the number of chain units belonging to the base polymer which participate in the β transition and their mean lengths are reduced by branching. This may explain the observed decrease of the height of the maximum damping. However, the lowering of the maximum damping temperature would indicate that an increase of mobility occurs in the main chain units of the base polymer as a result of grafting. This fact may be explained admitting that, because of the presence of frequent, long, rigid, polystyrene branchings, numerous voids are created in the structure, which lowers the interchain barriers opposing rotation around C—C bonds of the chain segments of the base polymer. In conclusion, the presence of frequent, long, rigid branches in the grafted structures, while causing a decrease of the total number of chain units of the base polymer participating to the motion and their mean lengths, renders more free those chain elements still capable of rotating, through an interchain separation which creates voids and lowers intermolecular forces.

The observed fact that in the temperature range between room temperature and T_g the value of dv/dT is lower for grafted materials than for the mixtures of the corresponding homopolymers may be connected with the fact that in the former the motions of polybutene units are not followed by complete softening of this component and curling of its molecules; this results in inhibition of its plasticizing action.

All comments just made concerning the polystyrene–polybutene system, are valid also for the SN–BN system. In the latter case, the transition at T_g' and the associated damping maximum are to be attributed to motions of main chain units of the base polymer (butadiene–acrylonitrile copolymer) and their positions depend on composition of the latter (Fig. 3);[7] the transition at T_g, however, is connected with the glass transition of the more rigid component (styrene–acrylonitrile).

From a comparison of the dynamic mechanical properties of the grafted SN–BN copolymers with those of mixtures of similar compositions, it can be observed that the shift of the glass transition of the base polymer, in this case, is much more marked than for the previously discussed polystyrene–polybutene graft system. This fact may be related to the polar character of the chain units of the base polymer. In fact, in butadiene–acrylonitrile copolymers the intrinsic flexibility of the chain is quite high, but the chain mobility is strongly limited by high intermolecular forces, due to the presence of polar —CN groups; so, lowering these forces through grafting, strongly enhances the chain mobility of the base polymer.

This point of view is supported also by the fact that, while in the mixtures the positions of both T_g' and of the damping maximum are very sensitive to

the composition (acrylonitrile content) of the base polymer, being shifted towards higher temperatures with increasing density of polar groups along the chain, in the grafted materials the positions of those characteristic temperatures, at least in the composition range explored by us, become practically independent of nitrile content of the polymer. In other words, in the grafted materials, the dipolar interactions are nearly cancelled out by the chain separation affected by branchings, and the small steric hindrance of CN groups on the chain mobility of the base polymer remains effective.

CONCLUSIONS

Although it is not possible to draw any conclusions of general character from so limited a series of experiments, these preliminary results however, have helped to elucidate some aspects of grafting, which must be common to any systems, and have demonstrated that the dynamic methods, in some cases, can be of valuable assistance in relating the mechanical behavior of a grafted material to its structure.

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Synopsis

Dynamic mechanical properties (sound velocity and damping factor) have been determined in samples of different polymeric mixtures and of corresponding grafted copolymers, at frequencies of the order of 10 kHz over a wide temperature range. In the mixtures the same relaxation phenomena, characteristic of each component, are found, located practically at the same temperatures (for a given frequency) as in the pure components. In the grafted materials, at contrary, if the degree of branchings is sufficiently high, the relaxation phenomena relative to the base component are shifted towards lower temperatures, as compared with the corresponding phenomena relative to the same component in the pure state or in mixture with the grafted component. These shifts are much more marked when the base component is characterized by polar chains or by hydrogen bridges between macromolecules. The experimental results are discussed and interpreted on the basis of the structure of the various components and of their interactions in the mixtures and in the grafted condition.

Résumé

Les propriétés mécaniques dynamiques (vitesse de son et facteur d'amortissement) ont été déterminées pour des échantillons constitués de divers mélanges de polymères, et de copolymères greffés correspondant, à des fréquences de l'ordre de 10 kHz sur une large gamme de température. Pour les mélanges, on retrouve les mêmes phénomènes de rélaxation caractéristiques de chaque composant, situés aux mêmes températures (pour une fréquence déterminée) que pour les composants purs. Pour les matériaux greffés,

par contre, les phénomènes de rélaxation relatifs au composant de base sont déplacés vers des températures plus basses, si on les compare aux phénomènes correspondants pour le même composant à l'état pur ou en mélange avec le matériel greffé. Ces glissements sont beaucoup plus fortement marqués lorsque le composant de base est caractérisé par des groupes polaires ou par des liaisons hydrogènes entre les macromolécules. Les résultats expérimentaux sont discutés et interprêtés sur la base de la structure des divers composants et de leurs interactions dans les mélanges et dans des compositions greffées.

Zusammenfassung

Die dynamisch-mechanischen Eigenschaften (Schallgeschwindigkeit und Dämpfungsfaktor) verschiedener Polymermischungen und der entsprechenden Pfropfcopolymeren wurden bei Frequenzen in der Grössenordnung von 10 kHz über einen weiten Temperaturbereich untersucht. In den Mischungen wurden dieselben, für jede Komponente charakteristischen Relaxationserscheinungen bei praktisch derselben Temperatur (für eine gegebene Frequenz) wie in den reinen Komponenten gefunden. Dagegen waren in den gepfropften Proben bei genügend hohem Verzweigungsgrad die Relaxationserscheinungen bezüglich der Grundkomponente zu niedrigeren Temperaturen verschoben, wenn jeweils die entsprechenden Erscheinungen bezüglich derselben Komponente in reinem Zustand oder in der Mischung mit denjenigen der gepfropften Komponente verglichen werden. Diese Verschiebung ist viel stärker ausgeprägt, wenn die Grundkomponente polare Ketten oder Wasserstoffbrücken zwischen den Makromolekülen enthält. Die experimentellen Befunde werden diskutiert und auf der Grundlage der Struktur der verschiedenen Komponenten und ihrer Wechselwirkung in den Mischungen und im gepfropften Zustand gedeutet.

Discussion

R. Buvet (*Paris, France*): Vous avez utilisé une méthode de résonance pour mésurer le module dynamique de vos échantillons. Je désiereais savoir si les courbes de dispersion thermique que vous avez données sont des courbes isofréquence au iso-forme de l'échantillon c'est à dire tracées à fréquence variable d'une température à l'autre. Dans ce dernier cas quel est l'écart maximal des fréquences de mésure, entre deux points de mesure.

E. Butta: The frequency was not constant; it varied some hundreds of cycles from the lowest temperature to the softening point.

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Grafts of Nylon and Unsaturated Acids

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One of the intriguing possibilities opened up by radiation-induced grafting is the preparation of polymers combining the hydrophobic properties of polyamides and hydrophilic properties of selected vinyl polymers.[1] The resulting graft polymers lend themselves to characterization in comparison to unmodified polyamides because modification occurs mainly in the amorphous areas of the polyamide substrate. As a result, tensile properties, such as tenacity and stiffness, which are functions of crystalline areas, are retained in the graft. On the other hand, properties which depend on amorphous areas, such as moisture regain and dyeability, are vastly changed. The purpose of this paper is to describe the preparation of typical hydrophilic grafts on polyamides, characterize their structure, and examine some of the unusual properties of these grafts.

The polyamide selected for this study was nylon 66 yarn prepared from adipic acid and hexamethylenediamine. The hydrophilic grafts were provided by two vinyl monomers: acrylic acid and maleic acid. These two acids lead to grafts covering a wide range of properties. Acrylic acid polymerizes readily and as a result forms grafts composed of long polymeric chains. Maleic acid, on the other hand, does not homopolymerize and gives short grafts. Nylon grafts with acrylic and maleic acid lend themselves to detailed study because these monomers diffuse readily into the nylon and the grafts retain the solubility characteristic of the nylon starting material. (Nylon–acrylic acid grafts are soluble in formic acid and benzyl alcohol in contrast to nylon–methacrylic acid grafts.[2]) Thus, well-developed analytical techniques can be applied for the characterization of these grafts. An important feature of acrylic and maleic acid grafts is their ability to give salts covering a wide spectrum of hydrophilic properties and also to give crosslinked ionic networks. This paper will be concerned mainly with the acid grafts as prepared, the sodium salts which are typical of hydrophilic grafts, and calcium salts which exemplify ionically crosslinked networks. The various techniques to prepare graft copolymers using ionizing radiation have been reviewed by Chapiro.[3]

Preparation of Grafts

Both maleic and acrylic acid were grafted to nylon by the direct radiation grafting technique where the fiber is irradiated while swollen in monomer.[3]

The maleic acid graft was prepared by soaking nylon yarns or fabrics in a 25% aqueous solution of maleic acid for one hour. The soaked yarns were then irradiated with 2 m.e.v. electrons from a Van de Graaff generator at dosages ranging from 2 to 60 Mrads. Excess acid was removed by washing with water at 70°C. Control of the amount of maleic acid grafted was achieved by the radiation dosage. The amount of maleic acid grafted measured by weight gain and titration of carboxyl groups in the grafted nylon is shown in Figure 1. The discrepancy between the titrated number of COOH groups and that measured by weight gain can be ascribed to the polyelectrolyte effect as the acid graft is converted to the sodium salt during titration.

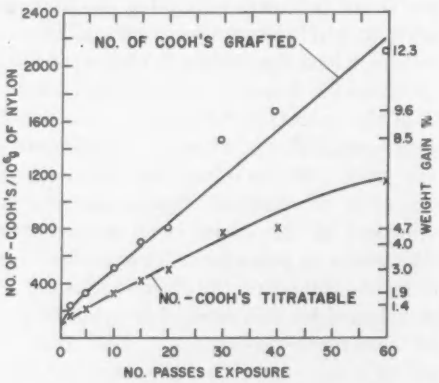


Fig. 1. Maleic acid grafted vs. radiation dose.

The acrylic acid graft was prepared by soaking nylon in aqueous acrylic acid. Control of the amount of acrylic acid grafted is achieved by adjustment of the concentration of the acrylic acid solution. The weight gain and the titratable COOH in the graft as a function of acrylic acid concentration is shown in Figure 2. Measurements of the diffusion coefficient of diffusion of aqueous acrylic acid into nylon have yielded a value of $D - 5 \times 10^{-9}$ cm.^{2}/sec. at room temperature with an activation energy of diffusion of 7.5 kcal., corresponding to a temperature coefficient of 1.5 for every 10°C. increase in temperature.[4] Diffusion rates are somewhat concentration dependent, faster penetration being observed at higher bath concentrations. Soaking times used were sufficient to reach equilibrium uptake of acrylic acid in nylon (10 min. for 15 dpf yarn at 26°C. from a 10% solution).

The sodium salts of the acrylic and maleic acid grafts were prepared by agitating grafted yarns or fabrics for one hour at 80°C. in a 1% aqueous solution containing twice the fabric sample weight of sodium carbonate. The calcium salts were prepared by agitating the sodium salts in a 1% solution of calcium acetate for one hour at 80°C.

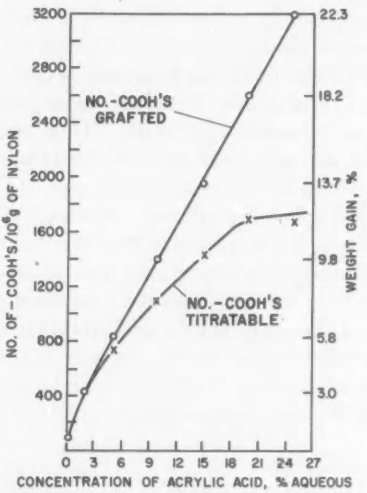
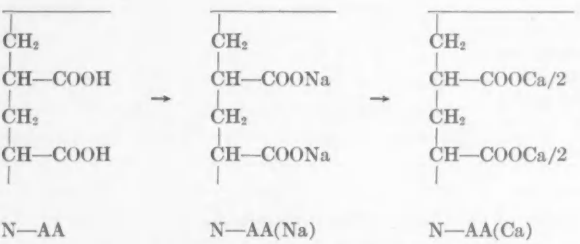


Fig. 2. Acrylic acid grafted vs. acrylic acid concentration.

The following nomenclature will be used in the rest of the paper to refer to the various salts: N—AA denotes acrylic acid graft on nylon; N—AA(Na) denotes the sodium salt of N—AA, and N—AA(Ca) denotes calcium salt of N—AA



Characterization of the Grafts

The structure of the maleic acid graft is relatively simple to determine, since maleic acid does not homopolymerize. The chain length is therefore one acid unit and the distribution of the grafted units on the nylon is directly related to the weight gain on grafting. For example, a graft containing 1000 COOH's per 10^6 g. of nylon (of 20,000 molecular weight) would have 10 maleic acid groups grafted, on an average, per nylon chain. The average distance between two maleic acid grafts would be a nylon backbone chain length of about 2000 molecular weight.

Weight gains of maleic acid on grafting reflect a high transfer from a grafted monomer unit to the nylon. According to Zimmerman,[5] the *G*

yield for radical production in nylon is about 6. Since grafting occurs only in the amorphous areas (about 50% of the nylon), the G yield is actually 3. On this basis 20 Mrad would give $3 \times 20 = 60$ radical sites/10^6 g. of nylon. The amount of maleic acid grafted corresponds to 1000 COOH's per 10^6 g. of nylon or 500 maleic acid units. Thus, each radical initiates a graft followed, on the average, by seven additional transfer reactions during the kinetic chain. From the effect of maleic acid on the extent of radiation-induced crosslinking and degradation following the procedure described by Zimmerman,[6] one is led to conclude that the mode of termination of radicals is predominantly disproportionation rather than combination. Therefore only very few covalent crosslinks would be expected.

Characterization of the nylon–acrylic acid grafts is more complex because of the homopolymerization tendency of the acrylic acid. We have determined the chemical composition, proportions, and molecular weights of the various components of the grafted product:

Nylon + Acrylic Acid Monomer →

Ungrafted Nylon + Ungrafted Polyacrylic Acid + N—AA

TABLE I
Composition of Nylon–Acrylic Acid Grafted Product (17.5% Weight Gain)

		Molecular weight	
	Weight-%	Number-average	Weight-average
Initial nylon substrate		17,400	
PAA homopolymer	1		
Nylon, ungrafted	52	13,500	
Nylon–PAA graft	45	37,000	
Nylon portion in graft	33	24,500	
PAA portion in graft	15	12,500	60,000

The results of the characterizations are shown in Table I. Separations were carried out for grafts of polyacrylic acid at two grafting levels: 17.5% and 32%. Results shown in the table pertain to the 17.5% graft. Note that the grafted product analyzed represents the final grafted fiber and not the crude product obtained immediately after irradiation. The fiber after the grafting step is washed with warm water. This treatment appears to be sufficient to remove all of the PAA homopolymer formed during the irradiation. Material balance run on the crude product shows that about 10–20% PAA homopolymer is formed during the irradiation step.

The separation scheme is outlined in Figure 3.

The polyacrylic acid homopolymer fraction is separated by solution of the graft in 90% formic acid and precipitation of the ungrafted nylon and graft copolymer by addition of water. The polyacrylic acid homopolymer fraction remains in solution.

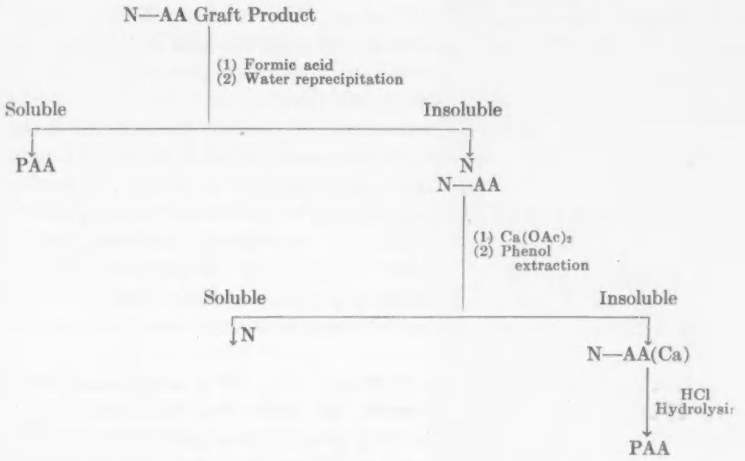


Figure 3.

Separation of Ungrafted Acrylic Acid Homopolymer. A 1 g. sample was placed in a glass-stoppered Erlenmeyer flask and 50 g. of 90% formic acid added. After complete solution of the sample, 50 ml. of water was added dropwise to the solution from a buret. The solution was stirred with a magnetic stirrer during addition of the precipitant. The final mixture was allowed to stand overnight at room temperature to accomplish complete precipitation of the nylon homopolymer and the N—AA graft copolymer. The precipitate was collected by filtration, washed free of acid, dried at 80°C. under vacuum, and weighed. The polyacrylic acid homopolymer content of the sample was calculated from the difference in weight between the final precipitate and original sample.

Curve *1* in Figure 4 is the precipitation curve for nylon in formic acid–water mixtures both in the presence and absence of polyacrylic acid. At a solvent composition of 27% water, nylon is completely soluble, but as the

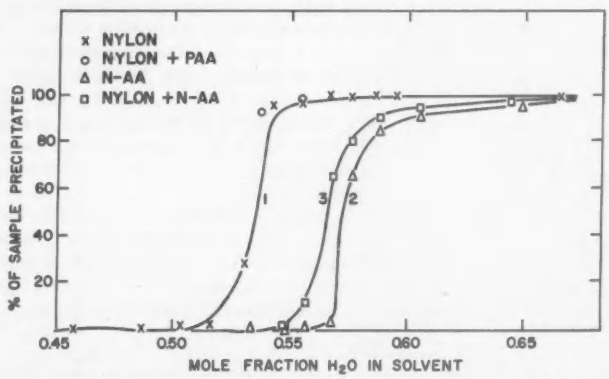


Fig. 4. Precipitation of nylon and nylon-acrylic acid grafts from formic acid solution.

water content is increased to 34%, precipitation becomes 99% complete. This tells us that nylon and polyacrylic acid in formic acid solution can be separated by precipitation of the nylon. The nylon precipitates quantitatively, leaving the polyacrylic acid in solution.

It is of interest to note that this separation is accomplished only if the coagulant is added to the polymer solution and not if the polymer solution is added to the coagulant. If nylon and polyacrylic acid in 90% formic acid is poured into water with rapid stirring, the polyacrylic acid is almost quantitatively coprecipitated with the nylon. Coprecipitation can usually be avoided by slow addition of the coagulant to the polymer solution. Precipitation occurs by a process of nucleation and aggregation of the insoluble phase which precipitates in essentially pure form, leaving the soluble materials in solution.

Curve *2* in Figure 4 is the precipitation curve for a sample of N—AA based on a 15% polyacrylic acid graft. It is seen that at a solvent composition of 34% water, which gives 99% precipitation with nylon, less than 1% of the N—AA graft is precipitated. On further addition of water a single fraction precipitates, eventually giving 98% recovery of the sample.

It was thought that nylon could be separated from the graft by control of the amount of water added as coagulant. When a mixture of nylon and N—AA graft is dissolved in formic acid, the two components coprecipitate according to curve *3*, indicating that no separation can be achieved by this method. A more effective way of separating the ungrafted nylon from the graft is by treating the mixture with calcium acetate. The calcium salt of the graft is insoluble in phenol at 80°C., while the ungrafted nylon is extracted.

Separation of Ungrafted Homopolymer and Graft Copolymer. A 6-g. sample was added to 200 ml. of 10% Na_2CO_3 solution and heated at 90°C. for 15 min. After washing free of carbonate with distilled water, the sample was heated at 90°C. for 15 min. in 10% $CaCl_2$ solution. The sample in the form of the calcium salt was washed free of chloride ion and dried at 50°C. under vacuum overnight. The sample was then combined with 30 ml. of phenol at 80°C. and stirred for 15 min. The mixture was filtered through coarse fritted glass and the residue pressed free of excess phenol. Extraction of the residue with fresh 30-ml. portions of phenol was repeated until a drop of the phenol extract no longer formed a precipitate when added to 10 ml. of acetone. The combined phenol extracts were added to a volume of acetone equal to ten times the volume of the extract. After precipitation was complete, the residue was collected by filtration and washed free of phenol with acetone. This phenol-soluble fraction was found by nitrogen and carboxyl analysis to be nylon homopolymer. The nylon homopolymer content of the original sample was calculated from the weight of this fraction.

The phenol-insoluble residue (graft copolymer) was washed free of phenol with acetone and converted to the free acid form from the calcium salt by heating at 90°C. with 200 ml. of 5% acetic acid solution. After washing free of excess acid with water, the product was dried to constant weight at room temperature in a vacuum desiccator over P_2O_5. The graft copolymer content of the original sample was calculated from the weight of this fraction.

The per cent polyacrylic acid in the graft is obtained from the weight gain of the nylon on grafting. The polyacrylic acid portion of the graft

is hydrolyzed away from the nylon by treatment with concentrated HCl at 100°C. The hydrolysis products are removed by dialysis, and the weight-average molecular weight of the polyacrylic acid is determined by viscosity of an aqueous solution of its sodium salt.

The number-average molecular weight of the nylon portion of the graft is calculated from that of the initial nylon 66 and of the ungrafted nylon 66. The number-average molecular weight of the polyacrylic acid is calculated from the molecular weight of the graft copolymer and the ratio of polyacrylic acid to nylon in the graft copolymer.

The high ratio of $\bar{M}_w$ to $\bar{M}_n$ for the polyacrylic acid grafts reflects a broader than expected molecular weight distribution. This can be accounted for by formation of free radicals on the polyacrylic acid as well as on the nylon substrate during the preparation of N—AA by the one-step grafting process.

If the irradiation is carried out at −80°C. on nylon presoaked in acrylic acid at room temperature, very little branching of polyacrylic acid is obtained. The ratio of weight-average to number-average molecular weight in this instance was 2.2.

Separation of Polyacrylic Acid Branches from Nylon Backbone of Graft Copolymer. An amount of graft copolymer containing 0.75–1.0 g. of polyacrylic acid was heated with 25 ml. concentrated hydrochloric acid in an evacuated sealed tube for a period of 20–24 hr. After cooling to room temperature, the sample was diluted with 25 ml. of water and placed in a cellophane dialysis tube. The sample was dialyzed for a period of 3 days in a stream of distilled water. The contents of the tube were transferred to a titration flask and titrated with standard NaOH to a thymolphthalein endpoint. The amount of polyacrylic acid present was calculated from this titration. The sample was then evaporated to a volume of about 40 ml. and 50 ml. 4*N* NaOH added. The final solution after dilution to 100 ml. was used for viscosity measurements to determine the molecular weight of the polyacrylic acid. Measurements made with known samples of nylon polymer and polyacrylic acid showed that this hydrolysis procedure caused complete degradation of the nylon without causing detectable degradation of polyacrylic acid.

Molecular Weight Measurements

The weight-average molecular weight of polyacrylic acid was calculated from viscosity measurements in sodium hydroxide solution.[7] The number-average molecular weight of the grafted polyacrylic acid was calculated from the number-average molecular weight of the graft copolymer and the weight of grafted polyacrylic acid per mole of graft copoly-

TABLE II

Sample	Weight gain, %	Molecular weight of grafted polyacrylic acid $\bar{M}_v$	$\bar{M}_n$	$\bar{M}_v/\bar{M}_n$
1[a]	17.6	60,000	14,000	4.3
2[b]	12.5	29,000	13,000	2.2

[a] Soaked in 20% acrylic acid solution at room temperature and irradiated at room temperature (1.5 Mrad).

[b] Soaked in 20% acrylic acid solution at room temperature, cooled to −80°C. and irradiated (1.0 Mrad), then allowed to warm to room temperature.

mer, assuming one polyacrylic acid branch per graft copolymer molecule. The molecular weight of nylon homopolymer was measured by viscometry in 90% formic acid solution.

The molecular weight of the graft copolymer was measured by osmometry using solutions of the trimethylphenylammonium salt of the graft copolymer in m-cresol. Results are shown in Table II.

It has been shown[8] that both termination and propagation reactions in this system are diffusion-controlled with the ratio of the rate constants $k_p/2k_t \simeq 1$. With this situation one would expect the grafted vinyl polymer to have $\bar{M}_w/\bar{M}_n \simeq 2$.

Properties of Nylon Grafts with Acrylic Acid and Maleic Acid

The acrylic and maleic acid grafts onto nylon showed marked differences from the starting nylon in hydrophilic properties, melting point, and recovery properties (Figs. 5–7). This discussion will be centered principally on these three properties.

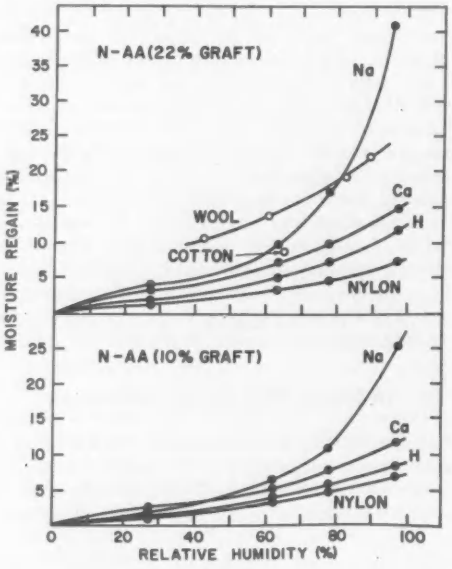


Fig. 5. Moisture regain of nylon-acrylic acid grafts.

Table III shows the yarn tensile properties of N—AA grafts. Tenacity (based on yarn starting denier) is not appreciably affected by the graft. The modulus is increased for the grafts in the acid and calcium forms because of H-bonding and ionic crosslinking. Conversely, the sodium salt of the graft has a lower modulus because of high moisture regain weakening H-bonding.

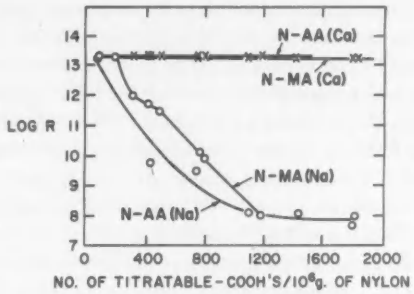


Fig. 6. Log R of acrylic and maleic acid grafts onto nylon.

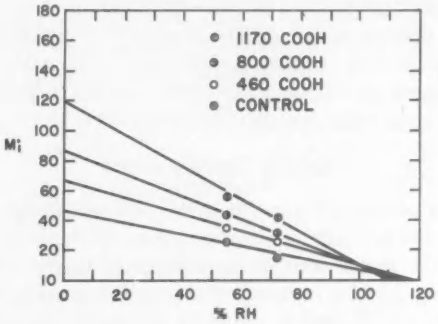


Fig. 7. Initial modulus vs. relative humidity for nylon–maleic acid grafted yarns (70 denier, 36 filaments).

TABLE III
Yarn Tensile Properties of N—AA Grafts

	Grafting, %	Tenacity, g./den.[a]	Elongation, %	Modulus, g./den.[a]	Radiation dose, Mrad
Nylon	0	5.4	28	14	0
N—AA	10	5.4	22	21	1
N—AA(Na)	10	4.7	32	7	1
N—AA(Ca)	10	5.2	24	18	1
N—AA	22	4.6	25	23	1
N—AA(Na)	22	4.0	31	7	1
N—AA(Ca)	22	5.1	27	27	1

[a] Based on denier of starting yarn.

Hydrophilic Properties

The hydrophilic properties as measured by moisture regain vs. relative humidity are shown in Figure 5. These data show that nylon fibers grafted with acrylic acid can match the moisture regain properties of wool and

cotton, depending upon the type of salt used and graft concentration. Closely related to moisture regain are the conductivity characteristics. These are measured by log R values, where R is the direct current resistance of the fiber measured in ohms at 25°C. and 50% RH. High values indicate a tendency to acquire and retain a charge and reflect high static propensity. Cotton has a log R of 11 under these conditions, whereas nylon is 13.3. Log R data for acrylic and maleic acid grafts in Na and Ca salt forms are shown in Figure 6. It can be seen that the antistatic properties of cotton can be matched with the grafted fibers in the sodium salt form.

Also related to hydrophilic properties is the dependence of fiber modulus on relative humidity. Introduction of additional carboxyl groups in nylon through grafting of maleic acid increases the modulus of the yarns. The increase is proportional to the number of carboxyl groups, but its effect becomes less pronounced as the relative humidity is increased. At 100% RH there is no difference in modulus between the grafted and ungrafted yarns. The relationship between modulus and relative humidity is shown in Figure 7. These results show that the modulus increase is a result of hydrogen bonds rather than covalent crosslinks.

Melting Characteristics

The acid form of the nylon grafts of acrylic and maleic acids have the same melting point and fiber melting characteristics as nylon. The x-ray crystallinity of the grafts is unchanged from the ungrafted fiber. This is an indication that grafting occurs in the amorphous areas without disrupting crystallinity. A change is noted in crystallite placement, however, suggesting a decrease in separation of crystallites.

Conversion of the grafts to the sodium or calcium form has a profound influence on the fiber melt temperature (determined by placing a yarn over an electrically heated tube and observing the temperature where the yarn breaks under the slightest load). Values are shown in Figure 8. The

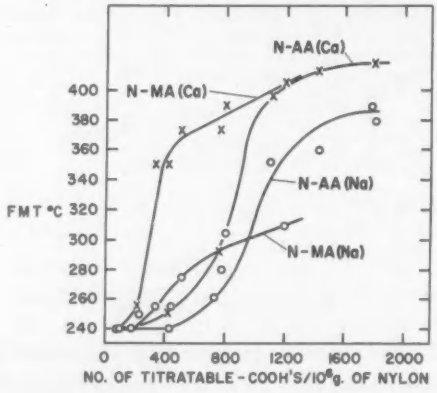


Fig. 8. Fiber melt temperature of acrylic and maleic acid grafts onto nylon.

fiber melt temperature is increased from 240°C. to over 400°C. for the calcium form of the acrylic acid graft. The sodium salts, while substantially better than nylon, are less effective than the calcium salts in raising fiber melt temperature. The divalent calcium salts provide a tighter, higher melting, crosslinked network. Increased fiber melt temperatures lead to increased hole melting temperature. For example, a glass bead heated to 300°C. dropped on a nylon fabric causes a hole. The calcium form of the acrylic acid graft is not melted by beads heated to a temperature as high as 600°C. The crystalline portions of the nylon in the graft melt at the usual melting point of nylon (260°C.), but the inorgano-organic framework of the amorphous areas remains infusible.

Recovery Properties

The dry recovery properties of nylon yarns or fabrics grafted with acrylic acid are not essentially different from those of ungrafted nylon. In the wet state, however, the picture is quite different. The crease recovery of the sodium salt of the acrylic acid graft rises sharply at high humidities to assume a value of 94% while wet as compared to 70% for unmodified nylon, the free acid form of the graft, or the calcium form. Figure 9 shows wet crease recoveries of wool, nylon, and nylon-acrylic acid graft fabrics as a function of relative humidity. The recovery of wool decreases with

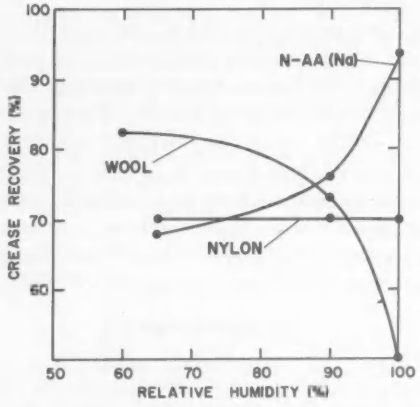


Fig. 9. Wet crease recovery of wool, nylon, and nylon–acrylic acid grafts vs. relative humidity.

RH in contrast to that of N—AA(Na). Creases formed in N—AA(Na) fabrics while dry are instantly removed upon immersion in water. In the conversion of the acrylic acid graft to the sodium form, the fiber undergoes a permanent degree of setting, termed Nasetting, which brings about an additional 8% shrinkage to the nylon fibers on top of the usual 10% boil-off shrinkage of nylon. The Naset fiber also has a more open structure and

is more permeable to finishing treatments, such as dyeing. Wrinkled fabrics, previously Naset under taut conditions, assume an ironed appearance upon wetting. Creases Naset into a fabric reappear as soon as the fabric is wetted out, even though the creases had been ironed out dry.

The high wet crease recovery of the sodium form of the acrylic acid graft has been explained in terms of ionic forces which come into play when the fiber is immersed in water. As in the case of polyelectrolytes, the salt groups are ionized and the polyacrylic acid side chains on the nylon backbone behave like anionic polyelectrolytes in which the electrical charges mutually repel each other, thereby extending the chains and resisting folds or other configurational restrictions. The calcium form of the graft does not have high wet crease recovery properties since calcium polyacrylate is insoluble in water and is not ionizable. The chain length of the grafted polyacrylic acid may play a role in determining the degree of crease recovery since the maleic acid graft, which is composed of short grafted chains, does not exhibit crease recovery of the same magnitude of the polyacrylic acid graft. A permanent change in fine structure is produced during the Nasetting treatment with the formation of microvoids throughout the polymer structure. These can be seen by examination of low-angle x-ray scattering of Naset fibers. The Naset structure as formed during the sodium carbonate treatment remains the same irrespective of the salt form of the graft. Wet crease recovery, on the other hand, is evident only in grafts in the sodium salt form.

The principles demonstrated on nylon grafted with acrylic and maleic acid have been extended to other hydrophilic and ionic monomers and polymeric substrates.[1] The same type of behavior has been noted with grafts of sodium styrenesulfonate on nylon. These grafts are hydrophilic and antistatic in both the sodium and calcium forms because the calcium salt of polystyrene sulfonic acid is soluble in water. These grafts also show increased resistance to hole melting and improved crease recovery. In general, grafting of a water-soluble vinyl polymer onto a hydrophobic polymer such as nylon is an effective means of increasing fiber hydrophile without changing the desirable tensile properties of the starting fiber.

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Synopsis

Nylon 66 has been grafted with maleic acid and acrylic acid. Maleic acid gives short grafts, while acrylic acid leads to grafts of long chains. Small doses (1 Mrad) are sufficient

to graft 10% acrylic acid, as compared to large doses (20–40 Mrad) for equivalent amounts of maleic. The proportions and molecular weights of the polyacrylic acid and nylon components of the grafts have been measured. The acrylic acid and maleic acid grafts on nylon fibers are readily converted to the corresponding sodium or calcium salts by treatment with sodium carbonate or calcium acetate. The various acid and salt forms are readily interconvertible. The sodium salts of the grafts are highly hydrophilic as measured by moisture regain, polymer conductivity, and antistatic properties. Fibers from sodium salt grafts give fabrics with high wet crease recovery properties. The sodium salt treatment, termed "Nasetting", provides a new type of setting treatment on nylon different from and additive to heat-setting. In contrast to nylon, the calcium salts of the grafts are infusible. The fiber melt temperature is raised from 250°C. to above 350°C., depending upon the graft level. Structure studies on these grafts show that polyacrylic acid is grafted throughout the bulk of nylon, principally in amorphous regions. There is no striking difference in crystallinity between unmodified nylon and the grafts. Structural changes in the fiber are seen during the Nasetting process.

Résumé

On a greffé sur du nylon-66 l'acide maléique et l'acide acrylique. L'acide maléique donne lieu à des greffages courts, tandis que l'acide acrylique donne de longues chaînes greffées. Des petites doses (1 Mrad) sont suffisantes pour greffer 10% d'acide acrylique, tandis qu'il faut des fortes doses (20–40 Mrad) pour obtenir des quantités équivalentes d'acids maléique. On a déterminé les concentrations relatives et les poids moléculaires des composants, acide acrylique et nylon, dans les polymères greffés. On peut transformer facilement les polymères greffés d'acide acrylique et maléique sur des fibres de nylon, en leurs sels sodiques et calciques correspondants, en les traitant par le carbonate de sodium ou l'acétate de calcium. Les différentes formes acide et sel sont facilement interconvertibles. Les sels sodiques des polymères greffés sont fortement hydrophiles, ce qu'on a mesuré par l'augmentation d'humidité, conductivité du polymère, et propriétés antistatiques. Les fibres des sels sodiques greffés donnent des produits caractérisés par de bonnes propriétés hygroscopiques. La transformation en sel sodique, appelée 'Nasetting' donne lieu à un nouveau type d'addition sur le nylon qui diffère et s'additionne au traitement à chaud. À l'encontre du nylon, les sels calciques des polymères greffés sont insolubles. La température de fusion de la fibre augmente de 250°C à 350°C suivant le dégrè de greffage. Des études de structure de ces polymères greffés montrent que l'acide polyacrylique est greffé dans la masse du nylon, principalement dans les régions amorphes. Il n'y a pas de différence notoire dans la cristallinité du nylon nonmodifié et des copolymères greffés. On a vu des différences de structure dans la fibre lors du processus de "Nasetting."

Zusammenfassung

Maleinsäure und Acrylsäure wurde auf Nylon-66 aufgepfropft. Maleinsäure gibt kurze Aufpfropfungen, während Acrylsäure zur Aufpfropfung langer Ketten führt. Kleine Dosen (1 Mrad) genügen um 10% Acrylsäure aufzupfropfen, hingegen benötigen äquivalente Mengen von Maleinsäyre grosse Dosen (20–40 Mrad). Der Anteil und das Molekulargewicht der Polyacrylsäure- und Nylonkomponente der Pfropfpolymeren wurden bestimmt. Durch Behandlung mit Natriumcarbonat oder Calciumcarbonat können die Acrylsäure- und Maleinsäureaufpfropfungen leicht in die entsprechenden Natrium- oder Calciumsalze umgewandelt werden. Die verschiedenen Säure- und Salzformen können leicht ineinander übergeführt. Die Natriumsalze der Pfropfpolymeren sind, gemessen an der Feuchtigkeitsaufnahme, Polymerleitfähigkeit und den antistatischen Eigenschaften, stark hydrophil. Fasern aus dem Natriumsalz des Pfropfpolymeren geben Gewebe mit guter Nassknitterfestigkeit. Die Natriumsalzbehandlung, "Nasetting" genannt, bildet ein neuartiges, von der Hitzebehandlung verschiedenes und

sie ergänzendes Verfahren. Im Gegensatz zu Nylon sind die Calciumsalze der Aufpfropfungen unschmelzbar. Die Schmeltztemperatur der Fasern steigt je nach dem Aufpfropfungsgrad von 250°C bis auf über 350°C. Strukturuntersuchungen an diesen Pfropfpolymeren zeigen, dass Polyacrylsäure in der ganzen Nylonmasse, hauptsächlich in den amorphen Bereichen aufgepfropft ist. Es besteht kein bedeutender Kristallinitätsunterschied zwischen nichtmodifizierten Nylon und den Pfropfpolymeren. Während des "Nasetting"-prozesses treten Strukturänderungen in der Faser auf.

Discussion

A. Parisot (*Institut Textile de France, Paris, France*): (*1*) Est-ce que le greffage a lieu dans l'ensemble de la fibre ou seulement dans les régions superficielles?

(*2*) Comment varie la résistance à la *flexion* des fibres greffées?

E. E. Magat: (*1*) Le greffage a lieu dans l'ensemble de la fibre.

(*2*) La résistance à la flexion n'est pas fortement changée par le greffage.

Dr. Goodman (*I.C.I. Ltd., Yorkshire, Great Britain*): I should like to ask Dr. Magat how stable the sodium ions in his salt-NAA grafts are towards the continued action of water or of mineral acids.

E. E. Magat: The sodium salts of the grafts behave as ion exchange resins of weak acids and as a result revert to the acid form under the influence of mineral acids or continued action of water. Hard water converts the grafts to their calcium form.

W. K. W. Chen (*A.M.F., Stamford, Conn.*): We have observed that when an ionic monomer is grafted to a crystalline polymer backbone, such as a fluorocarbon polymer, the resultant graft polymer (5–20% graft) has less alkaline stability than the original polymer. The stability of the original crystalline polymer appears to be impaired by increased accessibility of the alkaline reagents due to the presence of the grafted polyelectrolyte. Did you notice any loss of alkaline stability in acrylic acid-grafted nylon?

E. E. Magat: Acrylic acid-grafted nylon is substantially equivalent to unmodified nylon in terms of alkaline stability. Amide linkages in polyamides appear to be quite resistant to alkaline hydrolysis in spite of increased accessibility of the alkaline reagents.

J. Corbière (*Rhodiacéta, Lyon, France*): Il semble que dans le graphique illustrant la défroissabilité du Nylon en fonction de l'humidité relative il y aurait lieu d'introduire la notion de traitement thermique. On sait en effet que ces traitements ont une importance considérable sur l'infroissabilité du Nylon. Un nylon bien traité thermiquement devient plus défroissable que la laine et il y aurait donc lieu de préciser sur ce graphique (*a*) si le nylon témoin a été traité thermiquement (*b*) si oui, dans quelles conditions? (*c*) la courbe d'un nylon ayant subi un vaporisage sous pression dans les meilleurs conditions retenues pour assurer son infroissabilité.

E. E. Magat: Le nylon a été traité thermiquement a 180°C. pendant 2 min. En plus des conditions de traitement thermique, la defroissabilité depend des conditions d'essai. Le graphique compare la defroissabilité de la laine et du nylon utilizant le Monsanto crease recovery test. Dans d'autres conditions d'essai on a aussi vu que la laine peut etre inférieure au nylon en defroissage.

M. Sander (*Battelle Institut, Frankfurt, Allemagne*): Did you study the electrostatic behavior of the grafted nylon and if so, have you found parallelity between hydrophylic and electrostatic properties?

E. E. Magat: In the case of acrylic acid grafts on nylon, there was a parallelism between hydrophilic properties and freedom from static. The hydrophilic sodium grafts gave antistatic fibers. The parallel is, however, not applicable to all fiber modifications or treatments.

P. R. Thomas (*British Nylon Spinners Ltd., Pontypool, Great Britain*): Has the grafting any effect on the abrasion resistance of the yarn?

R. J. W. Reynolds (*Vinyl Products Ltd., Carshalton, Surrey, Great Britain*): Since the grafting of acrylic acid occurs throughout the nylon fiber, it would be interesting to know the solubility characteristics of the different acid graft copolymers in aqueous or nonaqueous methanol or ethanol. There might be some analogy with *N*-methylol nylons.

E. E. Magat: The grafts of acrylic acid on nylon are not soluble in methanol or ethanol. Solubility characteristics are quite different from *N*-methylol nylon because hydrogen bonding is not reduced in the grafts in contrast to *N*-substituted nylon. The grafts (in the acid form) are soluble in the same solvents as nylon-formic acid and phenols. It is of interest to note that grafts of methacrylic acid on nylon are not soluble in formic acid, in agreement with Roberts and Thomas.

M. Juillard (*Péchiney-Saint-Gobain, Aubervilliers, France*): Avez-vous étudié les propriétés obtenues avec les sels de métaux à deux ou plusieurs degrés d'oxydation tels que ceux de cuivre, par analogie avec les travaux du Prof. Kuhn sur les muscles d'acide polyacrylique?

E. E. Magat: On a preparé toutes sortes de sels des polymeres greffes y compris les sels de cuivre. Recemment Korschak a aussi préparé ces sels. On n'a pas fait d'études analogues aux travaux du Prof. Kuhn.

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Comportement des Fonctions Chimiques Introduites par Greffage à la Surface de Polymères Solides. I. Étude des Modifications de Structure Apportées par de l'Acide Polyacrylique Greffé à la Surface d'un Polyéthylène

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Quand on décrit la disposition des chaines d'un système macromoléculaire à l'état solide, on distingue habituellement entre phases cristallines et amorphes; mais on se contente, en général, si l'on exclut les phénomènes d'orientation, de décrire globalement l'état amorphe comme un agglomérat de chaines enchevêtrées.[1,2]

La complexité d'un tel enchevêtrement est telle que la différence entre deux structures possibles de l'état amorphe est considérée comme trop faible pour pouvoir se traduire par des différences de propriétés macroscopiques.

Si une telle description semble justifiée dans le cas de systèmes relativement simples constitués de chaines linéaires, non polaires, on concoit qu'il puisse en être autrement quand on considère, par exemple, un système macromoléculaire binaire au sein duquel la présence simultanée de deux types de chaines chimiquement différentes, ouvre de nouvelles possibilités de disposition mutuelle. Si, en particulier, une liaison chimique existe entre ces deux types de chaines, ce qui est le cas des copolymères greffés, on voit, à priori, que l'état amorphe "vrai" c'est-à-dire parfaitement désorganisé, n'existe pas puisque l'on impose une certaine répartition de chaines latérales A fixées sur un tronc B.

L'objet de la présente étude est de montrer que la phase amorphe d'un copolymère greffé donné peut effectivement se présenter sous différentes structures qui se manifestent par des propriétés différentes.

Des auteurs ont montré que les propriétés d'un polymère peuvent être influencées par l'ensemble des réactions chimiques dans lesquelles il s'est trouvé impliqué dans le passé.

C'est ainsi que Smets[3] a montré que l'acide polyacrylique est plus ou moins apte à se transformer en son polyanhydride suivant qu'il a été préparé par hydrolyse de ce polyanhydride acrylique[4,5] ou par la polymérisation simple du monomère. Il attribue ce phénomène à des différences d'ordre morphologique qu'on ne décèle pas par les méthodes d'analyse courante.

D'autres auteurs[6] examinant le cas de fibres de nylon, modifiées par le greffage de chaines latérales d'acide polyacrylique ont indiqué que le passage à la forme ionisée des groupements carboxyliques suivi d'un retour à la forme non ionisée s'accompagne d'une transformation irréversible des propriétés de tinctoriabilité. L'hypothèse selon laquelle la disposition mutuelle des chaines macromoléculaires d'un copolymère greffé est influencée par ce que nous appelons son "histoire chimique" semble donc vraisemblable.

Cette hypothèse implique, outre l'idée précédemment exposée de différents états dans le désordre des chaines, celle de l'irréversibilité de certains phénomènes qui interviennent dans les polymères à l'état solide.

On suppose que si l'on parvient à vaincre momentanément et au moins partiellement les obstacles à la mobilité des chaines (empêchements stériques, viscosité, forces de friction, etc.) et que l'on fige l'état obtenu en rétablissant les obstacles passagèrement abolis, la structure ainsi formée sera stable d'un point de vue physique, sinon thermodynamique.

Nous avons choisi d'étudier le cas du système constitué par un tronc polyéthylénique porteur de chaines d'acide polyacrylique introduites par greffage et nous nous sommes proposés d'étudier dans quelle mesure l'accomplissement d'un cycle réactionnel simple, portant sur l'activité des groupes carboxyliques, avec retour à l'état chimique initial, s'accompagnait d'un changement de structure.

Nous avons suivi les modifications chimiques subies par le système en caractérisant par spectroscopie infra-rouge les différents états des groupements carbonyles au cours des réactions qui mettent en jeu la fonction carboxylique. Des mesures de conductibilité superficielle et l'examen des échantillons par microscopie électronique, à chaque étape du cycle parcouru, ont permis de décrire certains aspects des transformations de structure correspondantes.

PARTIE EXPERIMENTALE

Les Echantillons

a. Leur Préparation

Le polyéthylène utilisé est du type "basse densité" ($d = 0{,}92$), en film de 0,03 mm d'épaisseur exempt de tout adjuvant. Nous avons procédé au greffage d'acide acrylique selon la méthode de préozonisation décrite par Landler et Lebel.[7]

Suivant le taux d'ozonisation, la durée et la température choisies pour la phase du greffage proprement dit, nous avons préparé des copolymères greffés de composition variable.

Les résultats présentés concernent un copolymère à 25% d'acide polyacrylique. Ce taux de greffage se rapporte au produit purifié par un lavage à l'eau suivi d'un séchage sous vide.

b. Les Traitements Chimiques

Opérant sur les échantillons de copolymère greffé ainsi préparés, nous avons étudié trois cycles de réactions destinés à faire passer, dans un premier temps, les groupements carboxyliques de la forme non ionisée à la forme ionisée et dans un deuxième temps, à retourner vers l'état initial non ionisé.

Cycle 1. Il s'agit, dans un premier stade, d'un traitement par une solution à 10% de potasse dans l'alcool éthylique. Ce traitement a été poursuivi pendant des temps s'échelonnant jusqu'à 2 h.30, à la température de 90°C.

Les échantillons, dans le deuxième stade, ont subi une attaque par l'acide chlorhydrique concentré à 90°C, pendant 5 minutes, afin de retourner aux groupes COOH non ionisés.

Cycle 2. Le permier stade consiste en un traitement par la triéthylène tétramine pure pendant 5 minutes à 90°C; il est suivi d'une attaque à l'acide chlorhydrique concentré pendant 45 minutes à 90°C qui permet le retour vers la forme non ionisée.

Cycle 3. Il commence par un traitement pendant Ih.30 par l'ammoniaque (22° Baumé) à 50°C et il est suivi d'un chauffage pendant 2 h.30 à 90°C qui détruit les sels instables d'ammonium avec retour aux groupements COOH non ionisés.

TECHNIQUES UTILISEES POUR L'ETUDE DES STRUCTURES

a. Spectroscopie Infra-rouge

Nous avons utilisé un spectrographe du type Perkin-Elmer Infracord. La méthode a consisté à relever et mesurer sur les spectres, les bandes caractéristiques afférentes aux différents états possibles du groupement carbonyle de la fonction carboxylique.

Bien que l'influence des groupements voisins sur les fréquences d'absorption des groupes carbonyles ne soit pas nettement élucidée, ainsi que le remarque Bellamy[8] et cela en particulier en ce qui concerne les perturbations apportées par la polymérisation de l'acide porteur des groupements carboxyliques, nous avons constaté que les fréquences caractéristiques des groupements CO rencontrés dans notre étude étaient suffisamment distinctes pour que de telles perturbations n'apportent pas d'ambiguité.

D'après Freeman[9] et Flett[10] nous avons attribué au groupement CO provenant d'un acide carboxylique non ionisé, la bande d'absorption qui apparait aux environs de 1720 cm^{-1}.

Les deux groupements CO des ions carboxylate $RCOO^-$, en raison de leur résonance donnent une bande d'absorption nouvelle à la fréquence de 1550 cm^{-1}.[11] Cross, Richard et Willis[12] ont d'ailleurs utilisé cette fréquence d'absorption dans leurs études des formes oxydées du polyéthylène.

Le groupement CO d'un anhydride à structure cyclique absorbe vers 1780 cm^{-1} ainsi qu'on l'a montré dans le cas de l'anhydride maléique.[13]

La proportion des groupes carbonyles présents sous telle ou telle forme a été déduite de l'intensité de l'absorption correspondante, selon la loi de Lambert-Beer:

$$kcd = \log (I_0/I)$$

où k = coefficient d'extinction du groupement considéré,
c = concentration en groupement CO de la forme étudiée,
d = épaisseur du film, et
I_0 et I sont les intensités avant et après absorption respectivement.

L'expérience montre que si un groupement CO d'une forme non ionisée (a) en concentration initiale c_a se transforme partiellement en une forme ionisée (b) de concentration c_b, nous pouvons toujours écrire la relation:

$$k_a c_a = k_b c_b + k_a(c_a - c_b)$$

ce qui signifie qu'à la précision de nos mesures, le coefficient d'extinction du groupe CO appartenant aux groupements carboxyliques est le même, quelle que soit la forme sous laquelle il se trouve dans le copolymère greffé que nous étudions.

Nous nous sommes donc limités à la mesure d'un facteur C proportionnel à la concentration vraie $\bar{c}$:

$$C = k\bar{c}$$

b. Conductibilité Superficielle

Nous avons utilisé une cellule de mesure de conductibilité adaptée à un "Iso R mètre" Lemouzy. Cet appareil donne une mesure ρ proportionnelle à la résistivité superficielle c'est-à-dire inversement proportionnelle à la conductibilité superficielle.

Le domaine de mesure s'étend jusqu'à des valeurs de égales à 10^{15} ohm-cm.

c. Microscopie Électronique

Nous avons utilisé un microscope du type JEM5Y. Nous avons examiné la surface des films traités en utilisant le procédé de double réplique. Une première empreinte a été prise avec un film d'acétylcellulose (Biodène) gonflé d'acétone.

Après évaporation du solvant une empreinte ombrée de ce film a été préparée par évaporation simultanée de carbone et de platine. Tous les clichés ont été pris avec un grossissement direct ($\times$ 10.000) sous une tension accélératrice des électrons de 80 kv.

RESULTATS

Cycle 1

Il s'agit du traitement potasse alcoolique–acide chlorhydrique. Sur la Figure 1 sont représentés les spectres d'absorption infra-rouge des différents

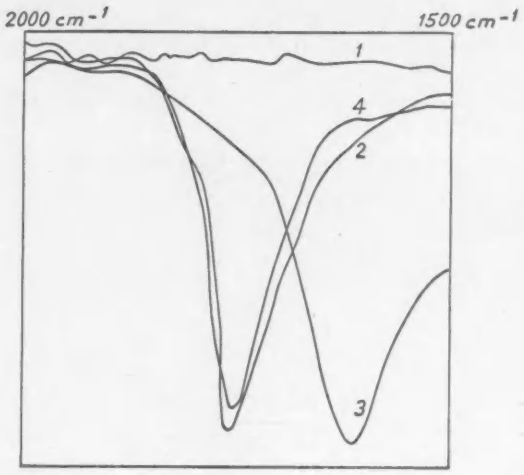

Fig. 1. Spectres d'absorption infra-rouge au cours du cycle de réactions 1: (*1*) polyéthylène non greffé; (*2*) polyéthylène greffé, non traité; (*3*) polyéthylène greffé, traité par la potasse alcoolique; (*4*) polyéthylène greffé, traité par la potasse alcoolique puis par l'acide chlorhydrique.

échantillons en fonction du traitement subi, pour les fréquences comprises entre 1500 et 2000 cm^{-1}. On remarque la présence d'une raie intense à 1720 cm^{-1} pour l'échantillon non traité. Cette raie diminue d'intensité après traitement à la potasse alcoolique tandis qu'apparait une raie à 1550 cm^{-1}. Après traitement à l'acide chlorhydrique, la raie à 1550 cm^{-1} disparait tandis que réapparait très intense, la raie à 1720 cm^{-1}.

Le Tableau I donne, pour chaque stade du traitement, la valeur des coefficients C et ρ précédemment définis.

TABLEAU I

Polyéthylène greffé	$C_{1720\ cm^{-1}}$	$C_{1550\ cm^{-1}}$	$\rho \times 10^{-13}$, ohm-cm
Non traité	450	0	12
Après traitement KOH alcoolique	13	436	3
Après traitement KOH alcoolique puis HCl concentré	460	0	11

L'examen au microscope électronique a montré que le greffage d'acide acrylique se manifeste par l'apparition, sur un fond uniforme, de pustules en grappes ayant un diamètre de l'ordre de 700–800 A (Fig. 2).

Des micrographies prises en cours de traitement par la potasse alcoolique montrent que la réaction se manifeste par un gonflement de ces pustules

qui semblent peu à peu se recouvrir d'un voile et qui au stade terminal n'apparaissaient plus individuellement qu'en de rares endroits (Fig. 3).

Le traitement à l'acide chlorhydrique fait disparaitre ce voile mais des globules volumineux apparaissent qui sont de dimensions nettement plus

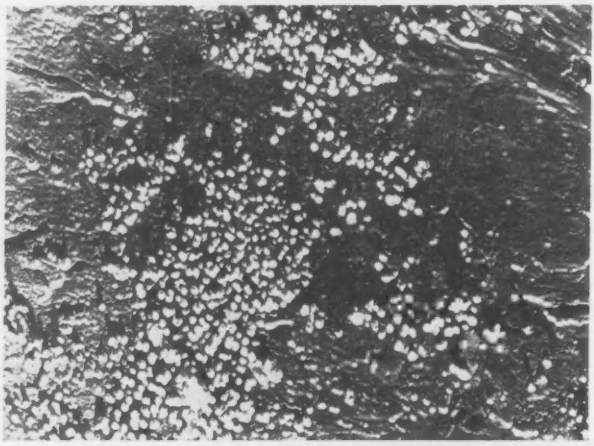

Fig. 2. Copolymère greffé, polyéthylène–acide polyacrylique. ×10.000.

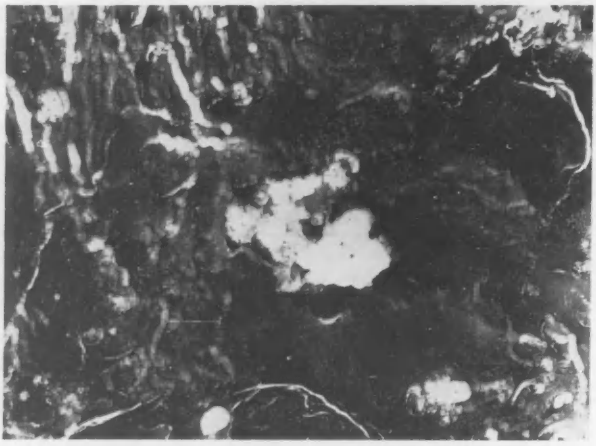

Fig. 3. Copolymère greffé traité par la potasse alcoolique. ×10.000.

importantes que les pustules initiales, leur diamètre moyen étant voisin de 1500 Å avec d'ailleurs une dispersion de ces dimensions plus grande qu'au stade initial (Fig. 4).

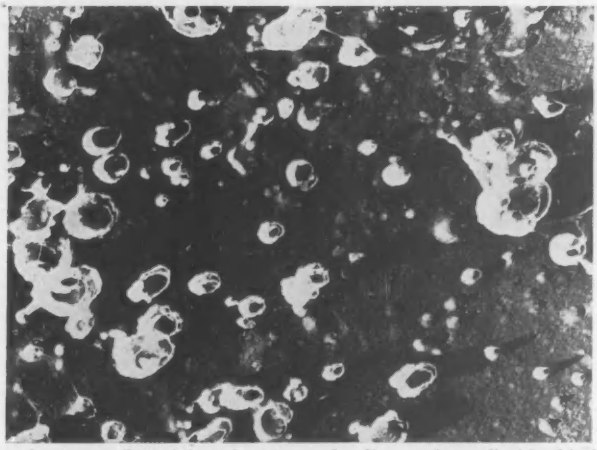

Fig. 4. Copolymère greffé traité par la potasse alcoolique puis par l'acide chlorhydrique. ×10.000.

Cycle 2

Il s'agit du traitement triéthylène tétramine–acide chlorhydrique. L'examen du spectre infra-rouge montre que, d'une part le passage à la forme ionisée (déplacement de la fréquence d'absorption de 1720 cm^{-1} à 1550 cm^{-1}) n'est pas total et que d'autre part la bande d'absorption à 1550 cm^{-1} est perturbée.

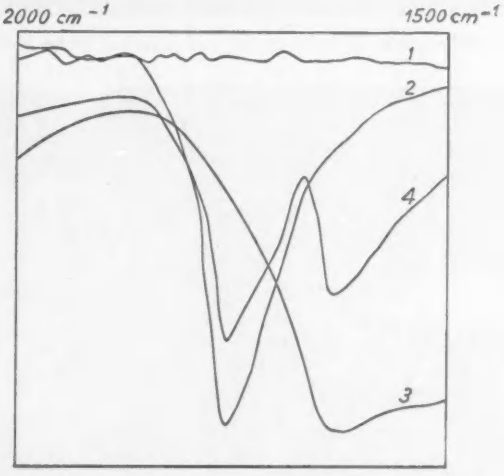

Fig. 5. Spectres d'absorption infra-rouge au cours du cycle de réactions 2: (*1*) polyéthylène non greffé; (*2*) polyéthylène greffé, non traité; (*3*) polyéthylène greffé, traité par la triéthylène tétramine; (*4*) polyéthyléne greffè, traité par la triéthylène tétramine puis par l'acide chlorhydrique.

TABLEAU II

Polyéthylène greffé	$C_{1720\ cm^{-1}}$	$C_{1550\ cm^{-1}}$	$\rho \times 10^{-13}$, ohm-cm
Non traité	530	0	12
Après traitement triéthylène tétramine	57	500	2,5
Après traitement triethylenetétramine, puis HCl concentré	450	115	8.4

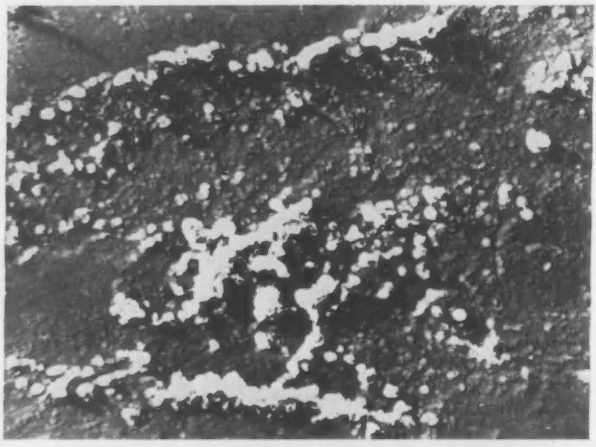

Fig. 6. Copolymère greffé traité par la triéthyèlne tétramine. ×10.000.

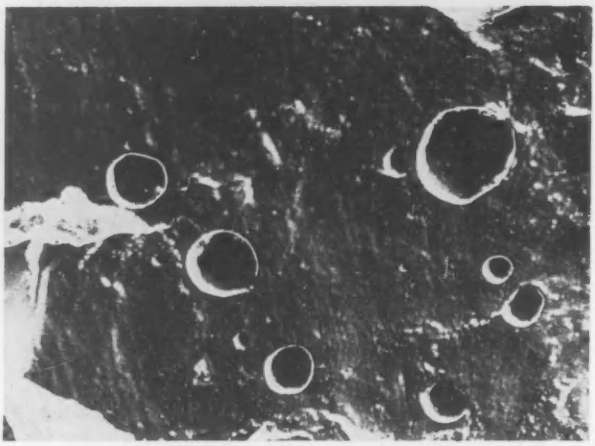

Fig. 7. Copolymère greffé traité par la triéthylène tétramine puis par l'acide chlorhydrique. ×10.000.

Après traitement prolongé (45 minutes) à l'acide chlorhydrique chaud (90°C), le retour à la forme initiale n'est pas total, c'est-à-dire qu'on retrouve les deux formes du groupement CO ainsi que le montrent la Figure 5 et le Tableau II.

La microscopie électronique montre que le traitement par la triéthylène tétramine se manifeste par une agglomération progressive des pustules d'acide polyacrylique greffé qui forment peu à peu un réseau de filaments allongés (Fig. 6).

Le retour à une forme partiellement non ionisée du groupement carboxyle s'accompagne de la formation de larges zones circulaires correspondant chacune à environ 20 à 30 pustules originale (Fig. 7).

Cycle 3

Il s'agit du traitement ammoniaque–chaleur. Le Tableau III et la Figure 8 résument les résultats obtenus par spectroscopie infra-rouge et conductibilité superficielle.

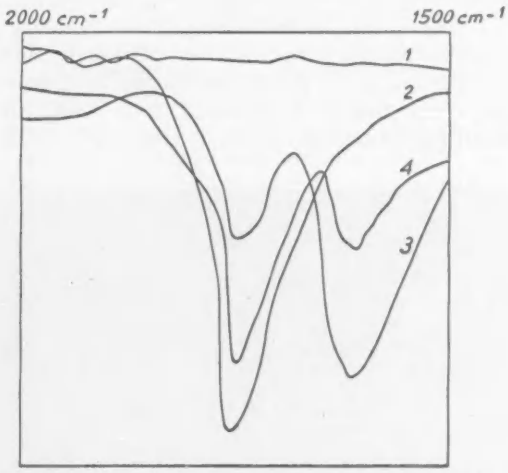

Fig. 8. Spectres d'absorption infra-rouge au cours du cycle de reactions 3: (*1*) polyéthylène non greffe; (*2*) polyéthylène greffé, non traité; (*3*) polyéthylène greffé, traité par l'ammoniaque; (*4*) polyéthylène greffé, traité par l'ammoniaque et soumis a un traitement thermique.

TABLEAU III

Polyéthylène greffé	$C_{1720\ cm^{-1}}$	$C_{1550cm^{-1}}$	$\rho \times 10^{-13}$, ohm-cm
Non traité	530	0	12
Après traitement ammoniaque	100	420	4
Après traitement ammoniaque puis thermique	460	73	6

Fig. 9. Copolymère greffé traité par l'ammoniaque. ×10.000.

Le microscope électronique a montré la perturbation totale apportée à la surface du polyéthylène greffé par la réaction de l'ammoniaque (Fig. 9) cependant que, d'une manière surprenante, toute trace superficielle de réaction disparait par traitement thermique (Fig. 10) bien que les spectres

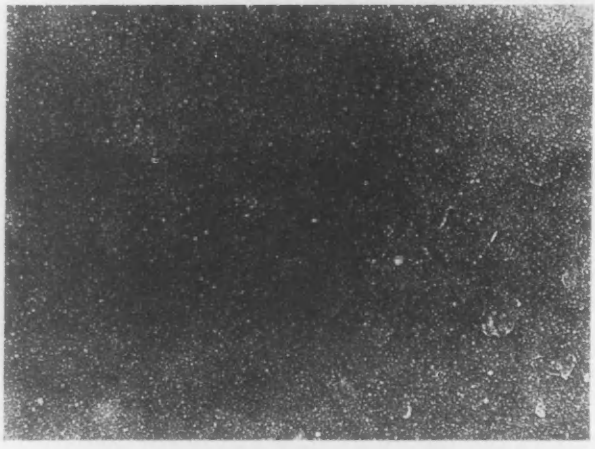

Fig. 10. Copolymère greffé traité par l'ammoniaque puis par la chaleur. ×10.000

d'absorption infra-rouge confirment que l'acide polyacrylique greffé est toujours bien fixé au tronc polyéthylènique. Ce résultats semblerait montrer que le greffage n'est pas seulement superficiel mais qu'il atteint aussi la masse du film.

DISCUSSION

L'examen des Tableaux I, II et III montre que seul le traitement à la potasse alcoolique est rigoureusement réversible quant au nombre de groupes ionisés et non ionisés.

En combinant les résultats de l'analyse par spectroscopie infra-rouge avec ceux des mesures de conductibilité superficielle, nous allons examiner dans quelle mesure les modifications de structure sont réversibles. Nous opérons de la manière suivante.

Nous admettons que la résistivité superficielle mesurée est composée de trois termes additifs qui sont respectivement: (*1*) la résistivité des éléments de surface du film de polyéthylène non perturbé par le greffage d'acide acrylique; (*2*) la résistivité dûe aux éléments de surface formés de chaines ou d'éléments de chaines d'acide polyacrylique greffé porteur de groupes carboxyliques non ionisés; (*3*) la résistivité dûe à des éléments identiques aux précédents mais à l'état ionisé.

$$\rho = \rho_A A + \rho_B B + \rho_P[1 - (A + B)] \qquad (1)$$

avec les conventions suivantes: ρ = résistivité superficielle de l'échantillon; ρ_P = résistivité superficielle des chaines de polyéthylène non perturbées par le greffage; ρ_A = résistivité superficielle des éléments d'acide polyacrylique porteurs d'un groupe carboxyle non ionisé; ρ_B = résistivité superficielle des éléments d'acide polyacrylique porteurs d'un groupe carboxyle ionisé; et A = concentration superficielle en éléments porteurs d'un groupe carboxylique non ionisé; B = concentration superficielle en élements porteurs d'un groupe carboxylique ionisé.

Par concentration superficielle en un élément donné, nous entendons la concentration en cet élément d'un film dont l'épaisseur tendrait indéfiniment vers zéro.

Les résistivités superficielles sont rapportées à une unité arbitraire de surface, définie par la cellule de mesure.

Pour un échantillon ayant un taux de greffage donné, nous pouvons écrire:

$$A + B = K$$

K étant une constante proportionnelle au taux de greffage.

Nous posons:

$$A/K = x$$

Les valeurs de x pour chaque état du produit étudié nous sont données par les concentrations relatives C mesurées par spectroscopie infra-rouge.

Pour un échantillon, dans un état déterminé, nous pouvons en effet écrire:

$$x = C_{1720}/(C_{1550} + C_{1720})$$

TABLEAU IV

Cycle réactionnel	Stade du traitement	x	C
Cycle 1	1. Echantillon non traité	1	450
(traitement à la potasse alcoolique)	2. Après traitement KOH alcoolique	0,03	449
	3. Après traitement HCl concentré	1	460
Cycle 2	1. Echantillon non traité	1	530
(traitement à la triéthylène tétramine)	2. Après traitement triéthylène tétramine	0,10	557
	3. Après traitement HCl concentré	0,79	565
Cycle 3	1. Echantillon non traité	1.	530
(traitement à l'ammoniaque)	2. Après traitement à l'ammoniaque	0,19	520
	3. Après traitement thermique	0,86	533

Ceci n'est évidemment valable que dans la mesure où la somme $C = C_{1550} + C_{1720}$ reste constante au cours des différents traitements de l'échantillon considéré.

Le Tableau IV montre qu'effectivement la constance de ce coefficient est réalisée à environ 5% près.

Les valeurs correspondantes de x sont indiquées pour chacun des cycles réactionnels considérés.

En écrivant ρ_A et ρ_B sous la forme suivante:

$$\rho_A = \rho_P - (\bar{a}/K)$$

$$\rho_B = \rho_P - (\bar{b}/K)$$

l'expression (1) se simplifie:

$$\rho = \rho_P - \bar{a}x - \bar{b}\,(1 - x)$$

Une mesure faite sur le polyéthylène non greffé donne:

$$\rho_P = 15$$

D'où finalement les trois relations:

$$\rho_A = 15 - (\bar{a}/K) \tag{2}$$

$$\rho_B = 15 - (\bar{b}/K) \tag{3}$$

$$15 - \rho = \bar{a}x + \bar{b}(1 - x) \tag{4}$$

Nous ne connaissons pas K, c'est pourquoi notre connaissance des résistivités ρ_A et ρ_B doit se limiter à celle des facteurs $\bar{a}$ et $\bar{b}$ définis par les relations (2) et (3) et calculés par la relation (4). Plus élevés sont ces coefficients, plus grande est la conductibilité superficielle correspondante.

Les mesures de conductibilité effectuée sur des films greffés mais non traités ($x = 1$) nous donnent immédiatement d'après (4):

$$\bar{a} = 3$$

Les mesures effectuées au deuxème stade de chaque traitement c'est-à-dire quand nous disposons de la forme ionisée, nous donnent alors $\bar{b}$. Nous

trouvons les valeurs $\bar{b}$ suivantes, selon le procédé utilisé pour ioniser les groupements carboxyliques: (*1*) traitement potasse alcoolique: $\bar{b}$ = 12,25; (2) traitement triéthylène tétramine: $\bar{b}$ = 13,55; (3) traitement ammoniaque: $\bar{b}$ = 12,9.

On remarque que les valeurs de $\bar{b}$ sont très voisines dans le cas des traitements 1 et 3 ce qui est normal étant donné que les propriétés de l'état ionisé ne devraient pas, à priori, dépendre de la réaction qui lui a donné naissance.

La valeur plus élevée trouvée dans le cas du traitement 2 semble prouver que la contribution des chaînons ainsi ionisés à la conductibilité superficielle de l'ensemble est accrue ce qui s'expliquerait par un étalement spécialement grand des chaînes latérales porteuses de groupements ionisés. On peut en effet penser que, dans tous les cas où les chaînes latérales d'acide polyacrylique sont porteuses de groupements polarisés de la même façon, les répulsions entre les différents segments d'une même chaîne entraînent un déplacement de celles-ci d'autant plus facile que la réaction se fait en milieu aqueux et que les éléments hydrophiles des chaînes d'acide polyacrylique sont gonflés et acquièrent ainsi une mobilité qu'elles n'avaient pas à l'état solide.

Simultanément avec leur déploiement, la propension des chaines d'acide polyacrylique greffées sur un tronc donné à s'enchevêtrer avec les chaines greffées sur un tronc voisin augmente.

Finalement, le passage de la structure non ionisée à la structure ionisée peut être schématisé selon la Figure 11.

Fig. 11. Le passage de la structure non ionisée a la structure ionisée (schematique).

L'amplitude du déploiement des chaînes peut être plus ou moins grande selon le milieu réactionnel qui les entoure, en raison des intéractions variables qu'elles peuvent échanger avec ce milieu.

Ceci explique sans doute les différences trouvées dans les valeurs calculées du coefficient $\bar{b}$ et en particulier la valeur plus élevée constatée dans le cas du cycle de réactions (2).

Cette extension des chaînes est bien mise en évidence par les micrographies électroniques des Figures 3, 6 et 9. On constate en effet, dans tous les cas, un gonflement des pustules d'acide polyacrylique et le déploiement progressif d'un voile qui les recouvre.

Admettant maintenant que les valeurs précédentes du coefficient de conductibilité $\bar{b}$ caractérisent l'état ionisé, nous pouvons calculer la nouvelle

valeur $\bar{a}'$ du coefficient de conductibilité $\bar{a}$ qui caractérise la structure non ionisée que l'on régénère au troisième stade de chacun des trois traitements étudiés. Si les phénomènes qui ont modifié la disposition des chaînes sont réversibles, nous devrons trouver: $\bar{a}' = \bar{a}$.

Pour calculer $\bar{a}'$, il suffit d'introduire dans l'équation (4) les valeurs précédentes de $\bar{b}$ et celles de x lues sur le Tableau IV.

Nous trouvons les valeurs suivantes: cycle 1 (potasse alcoolique): $\bar{a}' = 4$; cycle 2 (triéthylène tétramine): $\bar{a}'_1 = 15{,}4$; $\bar{a}'_2 = 4{,}75$; cycle 3 (ammoniaque): $\bar{a}' = 8{,}4$.

Rappelons que la valeur initiale de $\bar{a}$ était 3. Faisant abstraction, pour l'instant, du cycle 2, on constate que le coefficient de conductibilité des groupements non ionisés a augmenté par rapport à sa valeur initiale. Ceci s'explique facilement en reprenant le schéma de la Figure 11.

En effet, les enchevêtrements entre les chaînes déployées que l'on a obtenues à l'état ionisé ne peuvent être réversibles et une fois que les chaînons latéraux d'acide polyacrylique sont "noués," les forces de friction sont telles que l'annulation des forces de répulsion électrostatiques intramoléculaires ne peut entraîner leur rétraction. Nous avons ainsi "gelé" une structure particulière de l'état amorphe. Ceci est rendu possible par le fait que les équilibres thermodynamiques ne sont que pures abstractions dans le cas de polymères à l'état solide et que des états métastables représentent effectivement le cas le plus courant.

L'observation au microscope électronique confirme cette interprétation. La micrographie (Fig. 4) par exemple montre que les globules observés après retour à la forme non ionisée sont plus étalés qu'au stade initial, le rapport moyen des surfaces étant de l'ordre de 5.

Dans le cas du traitement 2, la valeur du coefficient de conductibilité élevée $\bar{a}'_1$ est obtenue après un traitement de 45 minutes dans l'acide chlorhydrique concentré. Il semble qu'elle serait dûe à la fixation chimique d'acide chlorhydrique avec formation d'ions ammonium quaternaires.

Si l'on prolonge le traitement on constate que peu à peu la conductibilité diminue pour finalement retomber à une valeur normale $\bar{a}'_2 = 4{,}75$.

La micrographie de la Figure 7 illustre l'aspect considérablement "gonflé" qu'ont pris les pustules initiales d'acide polyacrylique. Il semble qu'en moyenne 5 à 10 de ces pustules se sont agglomérées.

CONCLUSIONS

Nous avons mis en évidence l'étalement des chaines latérales porteuses de groupements carboxyliques quand ces groupements sont ionisés et montré que l'état ionisé dans un système macromoléculaire peut être différent suivant la réaction qui lui a donné naissance.

Par suite de l'irréversibilité de la nouvelle structure ainsi créée, nous avons montré que le retour à une forme non ionisée ne s'accompagnait pas d'un retour parallèle vers la structure initiale.

Cette interprétation des mesures de conductibilité superficielle associée à l'analyse par spectroscopie infra-rouge est confirmée par la microscopie électronique, nous amène à souligner l'importance de deux phénomènes: (*1*) la distinction possible entre divers états chimiquement identiques mais morphologiquement différents, au sein de la phase amorphe d'un système macromoléculaire condensé; (*2*) l'importance des phénomènes irréversibles, à l'état solide, et des états figés.

Des études en cours portant sur d'autres systèmes macromoléculaires devraient apporter un supplément d'information sur l'importance de ces phénomènes qui échappent aux interprétation de la thermodynamique classique.

Nous remercions Mlle Blanc et M. Gyeryga pour les mesures de conductibilité électrique et de spectroscopie infra-rouge, et Mlle Chauvel pour la microscopie électronique.

Nous remercions la Société Kléber-Colombes qui a autorisé la publication de cette étude.

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Résumé

On étudie l'influence qu'exerce sur la structure d'un polymère la présence de groupements réactifs dans le cas ou ces fonctions ont été introduites par greffage à la surface d'un polymère solide. La structure d'un tel polymère constitué d'un tronc de polyéthylène "basse densité" porteur de chaînons greffés riches en groupements chimiques réactifs (acide acrylique) est fonction de son histoire chimique. Cette histoire chimique se manifeste par une irreversibilité morphologique malgré la réversibilité apparente des modifications chimiques (ionisation des greffons d'acide carboxylique, suivie d'un retour à l'état non ionisé). Les réactions simples de la fonction acide sont étudiées en examinant, par spectroscopie infra-rouge, les bandes afférentes aux divers états du groupement carbonyle. Par des mesures de conductibilité superficielle, on étudie les structures qui correspondent aux divers stades de l'ionisation. Parallèlement, on suit au microscope électronique, le développement de ces nouvelles structures. Quelques cas de cycles réactionnels simples sont étudiés: traitements successifs par la potasse alcoolique et l'acide chlorhydrique; traitements successifs par la triéthylènetétramine et l'acide chlorhydrique; traitements successifs par l'ammoniaque, la chaleur. La combinaison des résultats de l'analyse spectroscopique et des mesures électriques montre que les

chaînons greffés d'acide polyacrylique, peuvent, à polarisation égale, présenter des structures différentes suivant qu'ils sont passés par l'état ionisé ou non. Des micrographies électroniques illustrent ce résultat. On interprète le phénomène en le considérant comme lié à la structure plus ou moins déployée des chaînons latéraux. A l'état initial, les greffons sont recroquevillés sur eux mêmes. Quand la succession des réactions chimiques fixe des groupements ionisés sur les sites préalablement occupés par les acides carboxyliques non ionisés, les chaînes latérales se déploient sous l'influence des forces de répulsion, qu'exercent entre eux les éléments de même polarité. Les chaînes latérales s'imbriquent les unes dans les autres, si bien que le retour à la forme acide non ionisée ne peut s'accompagner d'un retour à la configuration initiale des chaînes. On souligne l'importance des états métastables dans les systèmes macromoléculaires condensés et l'irréversibilité des phénomènes morphologiques.

Synopsis

The influence of the presence of reactive groups on the structure of a polymer has been studied by introducing such groups by grafting on the surface of a solid polymer. The structure of such a polymer, of which the trunk was a low density polyethylene carrying highly reactive side grafts (acrylic acid) is a function of its chemical history. Indeed irreversible morphologic changes can be stated, in spite of apparently reversible chemical modifications (as ionization of the carboxylic acid grafts, followed by back-neutralization to a non-ionic state). The simple reactions of the acid functions were studied by examining with infrared spectroscopy, the different bands corresponding to the various states of the carbonyl group. By measuring surface conductibility, the structures corresponding to the various states of ionization were studied. At the same time, these new structures were followed with an electron microscope. Some cases of simple reaction cycles are examined—successive treatments with alcoholic potassium hydroxide and hydrochloric acid,—successive treatments with triethylenetetramine and hydrochloric acid,—successive treatments with ammonia, and heat. The combination of the spectroscopic data with the electric measurements show that the polyacrylic acide side-grafts can, at equal polarization, present different structures, depending if they have passed through an ionized state or not. Electronic micrographs illustrate this result. This phenomenon is interpreted as being related with the more or less uncoiling of the side chains. In the initial state, the side grafts are coiled on themselves. When the successive chemical reactions ionize sites previously occupied by unionized carboxylic acid groups, the side chains uncoil on account of the repulsion forces of elements of the same polarity. The lateral chains are intricate in each other, in such a manner that a return to an unionized acid form cannot be accompanied with a return to the previous initial configuration. The importance of metastable states in condensed macromolecular systems is pointed out, as well as the irreversibility of morphologic phenomena.

Zusammenfassung

Der Einfluss der Gegenwart reaktiver Gruppen auf die Struktur eines Polymeren wurde durch Einführung solcher Gruppen mittels Aufpfropfung auf die Oberfläche eines festen Polymeren untersucht. Die Struktur eines solchen Polymeren, das aus einem Polyäthylen niedriger Dichte mit aufgepfropften, hochreaktiven Seitenzweigen (Acrylsäure) besteht, ist eine Funktion seiner chemischen Vorgeschichte. Tatsächlich können irreversible morphologische Äunderungen durch scheinbar reversible chemische Umsetzungen (wie Ionisierung der Carbonsäure-Aufpfropfungen und darauffolgende Rücktitration zum unionisierten Zustand) hervorgerufen werden. Die einfachen Reaktionen der Säurefunktion wurden infrarotspektroskopisch an den verschiedenen, den unterschiedlichen Zuständen der Carbonylgruppe entsprechenden Banden untersucht. Die den verschiedenen Ionisierungszuständen entsprechenden Strukturen wurden durch Messung der Oberflächenleitfähigkeit bestimmt. Gleichzeitig wurden

diese neuen Strukturen elektronenmikroskopisch betrachtet. Einige einfache Reaktionscyclen wurden untersucht: sukzessive Behandlung mit alkoholischer Kalilauge und Chlorwasserstoffsäure; sukzessive Behandlung mit Triäthylentetramin und Chlorwasserstoffsäure; sukzessive Behandlung mit Ammoniak und Hitze. Die spektroskopischen Daten gemeinsam mit den elektrischen Messungen zeigen, dass die Polyacrylsäureaufpfropfungen bei gleicher Polarisation verschiedene Strukturen aufweisen können, je nachdem, ob sie einen ionisierten Zustand durchlaufen haben oder nicht. Elektronenmikroskopische Aufnahmen dienen zur Illustration dieses Ergebnisses. Zur Erklärung wird eine stärkere oder schwächere Entknäuelung der Seitenketten angenommen. Im Ausgangszustand sind die Aufpfropfungen in sich selbst verknäuelt. Bei Ionisierung von Stellen, die früher durch nichtionisierte Carboxylgruppen besetzt waren, durch sukzessive chemische Reaktionen, entknäueln sich die Seitenketten wegen der Abstossung der Elemente gleicher Polarität. Die Seitenketten werden ineinander in einer solchen Weise verschlungen, dass eine Rückkehr zur nichtionisierten Säureform nicht von einer Rückkehr zur Ausgangskonfiguration begleitet sein kann. Auf die Bedeutung metastabilizer Zustände bei kondensierten markomolekularen Systemen sowie auf die Irrversibilität morphologischer Phänomene wird hingewiesen.

Discussion

P. Seidler (*Bellevue, France*): Est-ce que vous avez constaté dans vos expériences un greffage dans la profondeur de vos films? Nous avons travaillé avec un système analogue à savoir polytétrafluoroéthylène/acide acrylique. Avec des taux de greffage de 20% nous avons obtenu des films qui étaient entièrement greffés par le polyélectrolyte donnant ainsi des membranes échangeuses d'ions.

C. Job: Nos résultats sont en accord avec les vôtres puisque diverses éstimations indiquent qu'un pourcentage elevé (jusqu'à 80%) de l'acide polyacrylique greffé se trouve effectivement dans la masse, même quand le greffage a eu lieu en phase vapeur, ce qui est le cas du copolymère étudié dans le travail présenté. Une telle éstimation a pu être faite à partir de mesures effectuées sur des micrographies électroniques.

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Étude Rheologique de Copolymères Greffés à Base de Polychlorure de Vinyle et de Copolymère Styrolène–Anhydride Maleique

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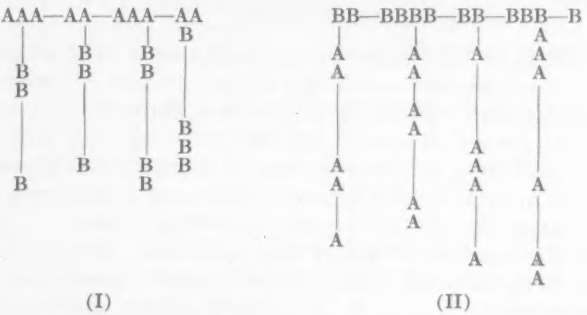
BUT DE L'ETUDE

Lorsque l'on considère un copolymère greffé constitué de deux monomères A et B, on peut préparer toute une série de copolymères variant en composition.

Mais, pour une composition donnée, il est possible d'imaginer deux types de structure fondamentale correspondant aux deux schémas (I et II):



(I) (II)

c'est-à-dire que deux produits de même composition peuvent être obtenus par greffage de A sur B ou par greffage de B sur A. Deux types de copolymères inversés sont donc accessibles.

Si maintenant, on considère l'un des types de greffés, on imagine que la même composition globale peut être obtenue par une gamme de produits intermédiaires entre ceux ayant peu de greffons très longs, et ceux ayant beaucoup de greffons courts. Ce facteur de répartition correspond à la structure topochimique du copolymère greffé.

Donc un copolymère greffé est au moins caractérisé par trois éléments: (*1*) la composition chimique; (*2*) le sens de greffage; (*3*) la structure topochimique.

Le but de cette étude est de déterminer comment ces trois variables interviennent sur les propriétés rhéologiques.

On trouve déjà quelques tentatives de détermination de ces relations, mais elles ont tantôt porté sur la composition et la structure topochimique

sans examiner l'influence du sens de greffage[1,2] tantôt porté sur un nombre d'expériences trop faible pour qu'une loi puisse en être déduite.[3]

Dans le cadre de cette étude, on a examiné le point de transition de second ordre et l'écoulement visqueux mesuré aux températures élevées sur les polymères à l'état condensé.

Le monomère A est le chlorure de vinyle dont le polymère a un point de transition de second ordre relativement bas et une énergie d'activation de viscosité basse tels que déterminés dans cette étude.

Le monomère B est en fait une alternance de styrolène et d'anhydride maléique et dont l'alternance au cours de la copolymérisation est sensiblement 1:1.[4,5]

En réalité, dans le cadre de cette étude, les résultats analytiques prouvent que l'on a obtenu 1,07 mole de styrolène pour 1 mole d'anhydride maléique soit sensiblement ce rapport 1:1.

L'étude est complétée par la comparaison des copolymères avec des mélanges des deux polymères constitutifs des copolymères greffés, ces mélanges étant préparés selon plusieurs techniques.

PREPARATION DES COPOLYMERES GREFFÉS

Greffage sur Polychlorure de Vinyle

Le polymère de base utilisé est un produit commercial polymérisé en suspension, se présentant sous forme de poudre dont les grains sont un agglomérat de grains plus fins et qui a l'intérêt d'être dépourvu de savons. Sa masse moléculaire est voisine de 75.000.

On a ozonisé 400 g de polymère, sous un courant d'oxygène sec de 450 l/h sous une pression de 1,050 kg/cm^2 et contenant 18 mg d'ozone par litre.

L'ozonisation est effectuée pendant des temps variables. Ces temps variables d'ozonisation entraînent des écartements variables des points d'attaque du polymère par l'ozone et ce sont eux qui détermineront l'écartement des greffons.

Les conditions de décomposition thermique des produits d'ozonisation du polychlorure de vinyle sont connues[6] et obéissent à la loi

$$k_d = 1{,}6 \times 10^8 e^{-19.750/RT}$$

Cette loi régit les conditions de greffage du mélange styrolène–anhydride maléique.

Pour le greffage, pour des teneurs en polychlorure de vinyle au moins égales à 50% en poids du mélange final, le styrolène et l'anhydride maléique sont dissous dans le chloroforme et dispersés sur le polychlorure de vinyle.

Le chloroforme est ensuite évaporé et la polymérisation est effectuée par chauffage sous vide pendant 2 heures à 100 °C.

Pour des teneurs en polychlorure de vinyle inférieures à 50% en poids, l'anhydride maléique est dissous dans le styrolène à 70 °C et la solution est dispersée sur le polychlorure de vinyle pulvérulent, placé sous vide et chauffé pendant 2 heures à 100 °C.

Pour un mélange contenant 90% de monomères, la polymérisation démarre dès la dispersion des monomères sur le polychlorure de vinyle et étant exothermique échauffe suffisamment le mélange pour se propager seule en un temps très court.

Dans tous les cas, la polymérisation est pratiquement totale.

Les copolymères greffés obtenus sont débarrasés des faibles quantités de monomères résiduels par des lavages au chloroforme.

Greffage sur Copolymère Styrolène–Anhydride Maléique

Il faut avant tout préparer le copolymère. Parmi différents systèmes étudiés, la technique suivante a été retenue.

Une solution composée de styrolène distillé (72,8 g), anhydride maléique (68,6 g), peroxyde de benzoyle (0,707 g), et chloroforme (700 ml) est préparée.

Sous vide, en autoclave, cette solution est chauffée pendant 2 heures à 60°C. Le rendement de polymérisation dans ces conditions est de 90%.

Le copolymère formé étant insoluble dans ce milieu de polymérisation est précipité sous forme d'une poudre très fine qui est débarrasée des fractions restantes de monomères par lavages au chloroforme.

Le polymère pulvérulent est ozonisé à raison de 200 g sous un débit d'oxygène de 450 l/h sous une pression de 1,050 kg/cm^2 et contenant 18 mg d'ozone.

Pour obtenir des écartements différents de points d'attaque par l'ozone, on ozonise pendant des temps variables.

Ces points d'attaque d'écartements différents entraîneront la formation de greffons d'écartements différents. L'écartement des greffons est donc réglé par les conditions d'ozonisation.[1]

L'étude cinétique de la décomposition thermique des produits d'ozonisation de ce copolymère styrolène–anhydride maléique, étudiée dans le cadre de ce travail conduit à la loi:

$$k_d = 3{,}4 \times 10^5 \, e^{-15.500/RT}$$

L'énergie d'activation très faible obtenue est différente de celles obtenues sur des produits péroxydiques d'autres polymères neutres où l'on trouve des valeurs entre 25 et 30 kilocalories[1,7] mais est à rapprocher de celles obtenues pour des polymères acides[6–8] qui est entre 15 et 20 kilocalories. Or l'anhydride maléique est toujours partiellement hydrolysé. Le greffage de chlorure de vinyle sur le copolymère styrolène anhydride maléique est effectué en autoclave à température assez basse pendant de longues durées à savoir pendant 192 heures avec élévation de la température par paliers entre 25°C et 55°C.

Le rendement de greffage reste faible. La proportion de chlorure de vinyle greffé par rapport à la quantité introduite ne dépasse guère 50% pour de faibles additions de monomère et tombe en dessous de 10% pour de fortes additions de monomères.

En outre, pour un taux d'ozonides donné, il y a une limite de greffage de chlorure de vinyle, d'autant plus élevée que la teneur en ozonides est forte.

Dans le cadre de cette étude, pour les plus faibles taux d'ozonisation, la quantité maximum de chlorure de vinyle qui a pu être greffée est de 20% du copolymère greffé final.

Pour les taux d'ozonisation les plus élevés, cette limite se déplace à 75% du copolymère greffé final.

Après polymérisation, le copolymère greffé est débarrassé du chlorure de vinyle résiduel par simple évaporation de celui-ci.

Fractionnement des Copolymères Greffés

Au cours du greffage, étant donné que les produits d'ozonisation des polymères ne contiennent pas d'hydroperoxydes, il n'y a pas de formation de radical OH. Il n'y a donc pas de source importante de formation d'homopolymère.

Toutefois, les réactions de transfert peuvent être la cause de cette formation d'homopolymère formé.

La méthyl éthyl cétone peut être considérée comme un solvant préférentiel du polychlorure de vinyle et les solutions aqueuses ammoniacales sont des solvants selectifs du copolymère styrolène–anhydride maléique.

En effectuant des fractionnements sur les deux types de copolymères greffés, et à l'aide des deux solvants, on n'obtient aucune fraction qui ne soit pas soluble au moins dans l'un des deux solvants. Ceci indique qu'il n'y a pas de réticulation au cours du greffage.

Le fractionnement est donc effectué en prélevant deux échantillons de copolymère greffé. Sur l'un d'eux, on procède à une extraction à la méthyl éthyl cétone et l'on obtient deux fractions dont l'une est soluble et l'autre insoluble.

Sur l'autre échantillon, on procède à une extraction par une solution aqueuse ammoniacale. Sur chaque copolymère greffé, on se trouve donc en présence de quatre fractions.

Les analyses chimiques prouvent que ces quatre fractions sont en fait constituées de chlorure de vinyle et de styrolène-anhydride maléique.

En fait, on sépare surtout d'une part les chaînes courtes de styrolène–anhydride maléique associées à des chaînes longues de polychlorure de vinyle et d'autre part les chaînes longues de styrolène–anhydride maléique associées à des chaînes courtes de polychlorure de vinyle, comme l'ont montré dans d'autres cas Bamford et White.[9]

En conséquence, les copolymères greffés ont été utilisés pour l'étude, sans autre purification que l'élimination des fractions de monomères non polymérisées.

En fait, quelques copolymères greffés ont été examinés en les débarrassant des produits riches en styrolène–anhydride maléique et les résultats obtenus prouvent qu'il n'y a pas de différence notable en variation de point de transition de second ordre entre un copolymère fractionné et un co-

polymère non fractionné de même mode de préparation, à composition chimique finale identique.

Préparation des Mélanges

Les caractéristiques doivent être comparées à celles obtenues pour les mélanges des deux polymères constitutifs des greffés, c'est-à-dire le polychlorure de vinyle et le copolymère styrolène–anhydride maléique.

La comparaison n'est établie qu'avec des mélanges dont la composition avoisine 50:50.

Par contre, plusieurs procédés ont été adoptés pour la préparation de ces mélanges.

Mélange A. Le polychlorure de vinyle pulvérulent est dispersé dans une solution du copolymère styrolène–anhydride maléique dans le tetrahydrofurane et l'ensemble est séché. Dans ces conditions, l'un des polymères est très divisé et l'autre moins.

Mélange B. Ce mélange est l'inverse du précédent. La poudre du copolymère est dispersée dans une solution de polychlorure de vinyle dans le tetrahydrofurane.

Mélange C. Ce mélange est un simple mélange mécanique à sec et à froid des poudres des deux polymères. De tous les types de mélange, il est théoriquement le plus hétérogene.

Mélange D. Les deux polymères sont mélangés sur un mélangeur à cylindresvers 200°C. Dans ces conditions, les deux polymères sont amenés en contact, à l'état fondu.

Mélange E. Dans ce cas, le copolymère styrolène–anhydride malèique est dissous dans une solution ammoniacale aqueuse et mélangé avec un latex de polychlorure de vinyle et l'ensemble est séché.

Dans ce cas, les deux polymères sont très dispersés et aucune demixion n'est possible.

Dans ce cas, par l'ammoniaque, l'anhydride est transformé en sel d'ammonium mais au moment du moulage, le sel d'ammonium est décomposé et régénère l'anhydride, ce qui a pu être vérifié par études spectrales en Infra-rouge. C'est un procédé connu pour obtenir des mélanges de polymères très finement dispersés.[10]

RESULTATS EXPERIMENTAUX

Possédant les deux polymères troncs, avec les differentes conditions d'ozonisation utilisées et les différentes conditions de greffage, on dispose d'une série de copolymères greffés variables en composition, en écartement de greffons et en sens de greffage.

Sur ces polymères on mesure la variation du module de torsion en fonction de la température.[11]

On mesure en outre, les caractéristiques d'écoulement visqueux dans différentes conditions de température, ce qui doit permettre de déterminer l'énergie d'activation de l'écoulement visqueux.

Le Module de Torsion

Celui-ci est déterminé en appliquant un couple de torsion à une éprouvette parallèlipipédique. Il est exprimé en kg/mm².

On étudie l'évolution de ce module en chauffant le matériau à la vitesse régulière linéaire de 1,2°C/min.

Ce module de torsion pour les polymères rigides varie peu entre la température ambiante et le point de transition de second ordre apparent de ce polymère. Lorsque l'on atteint la température correspondant au point de transition apparent, le module décroit très rapidement. En suivant donc l'évolution du module de torsion en fonction de la température, il devient possible de déterminer une valeur du point de transition de second ordre apparent.

La température de décroissance rapide du module de torsion se situe vers 80°C pour le polychlorure de vinyle.

Pour le copolymère styrolène–anhydride maléique le comportement thermique est tel que le produit n'est moulable qu'à des température très élevées. Seules des compositions greffées très pauvres en polychlorure de

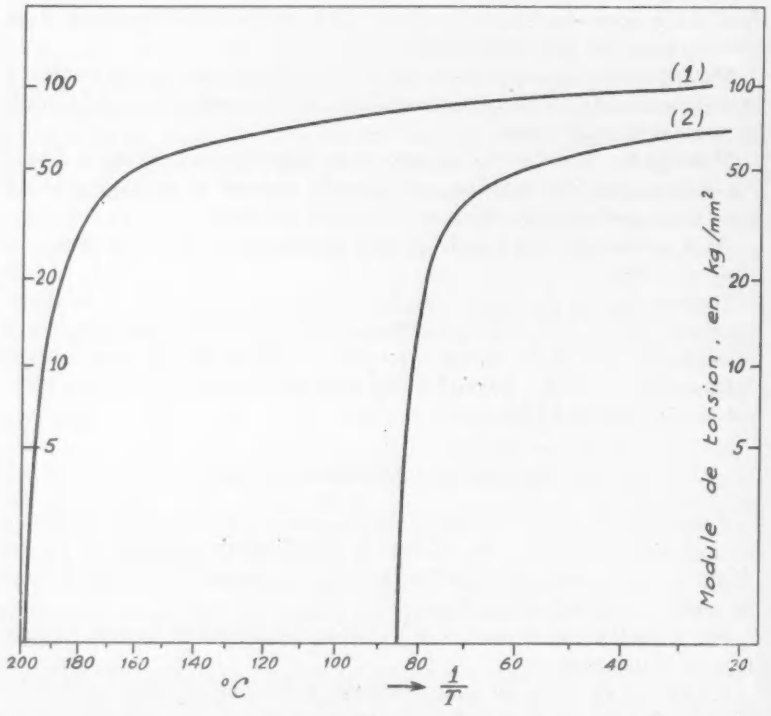


Fig. 1. Modules de torsion: (*1*) copolymère styrolène–anhydride maléique; (*2*) polychlorure de vinyle.

vinyle sont utilisables et elles permettent de conclure que le copolymère styrolène-anhydride maléique a un point de transition de second ordre supérieur à 200°C.

La Figure 1 montre les courbes de torsion du polychlorure de vinyle et d'un copolymère greffé contenant 92% de styrolène–anhydride maléique.

Les courbes de torsion se présentent tantôt avec un seul point de fléchissement, tantôt avec plusieurs points de fléchissement dont le plus bas se situe en général à 80°C (Fig. 2).

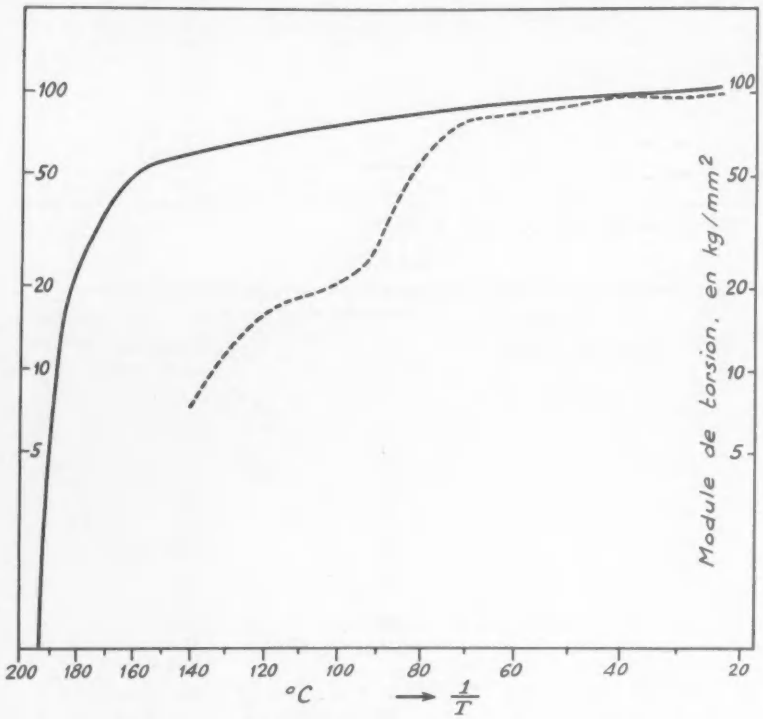


Fig. 2. Modules de torsion de copolymères greffés: (——) 9,15% chlorure de vinyle; (- -) 22,6% chlorure de vinyle.

Ce premier point correspond au polychlorure de vinyle.

En fait, on compare, pour les différents produits, la température à laquelle le module de torsion a considérablement décru, et on choisit la température à laquelle ce module tombe à 10 kg/mm². Cette température particulière est choisie pour avoir une comparaison valable entre les différents produits.

Les résultats sont rassemblés dans les Tableaux I et II et sur les Figures 3 et 4.

TABLEAU I
Greffage de Styrolène–Anhydride Maléique sur Polychlorure de Vinyle: Point de Transition de Second Ordre[a]

Teneur en ozonides, mole × 10^{-4}/g de polymère	Teneur en PVC, %	Température de module (10 kg/mm²), °C.
0,15	73	91
	91	85
	97	83
0,37	57	100
	76	83
	91	80
0,74	13	183
	30	137
	56	97
	95	85
1,18	60	97
	79	80

[a] Mesuré par variation du module de torsion.

TABLEAU II
Greffage de Chlorure de Vinyle sur Copolymère Styrolène–Anhydride Malèique: Point de Transition de Second Ordre[a]

Teneur en ozonides, mole × 10^{-4} g de polymère	Teneur en PVC, %	Température de module (10 kg/mm²), °C.
1	82	198
	92	188
	25	174
2,5	25	180
	40	125
	49	103
5,2	44	118
	54	90
	69	88
10	24	164
	33,5	130
	38	124
	59	91
	67	90

[a] Mesuré par variation du module de torsion.

Chaque couple "tableau-figure" se rapporte à un sens de greffage différent.

Les valeurs obtenues pour quelques mélanges sont portées sur la Figure 3 et sont en fait pour la température de module de torsion égal à 10 kg/mm²: mélange A (50% PVC) 90°C; mélange B (50% PVC) 81°C; mélange C (50% PVC) 87°C; mélange D (50% PVC) 85°C; mélange E (63% PVC) 92°C; mélange E (35% PVC) 106°C; greffé (extrapolé) (50% PVC) 107°C

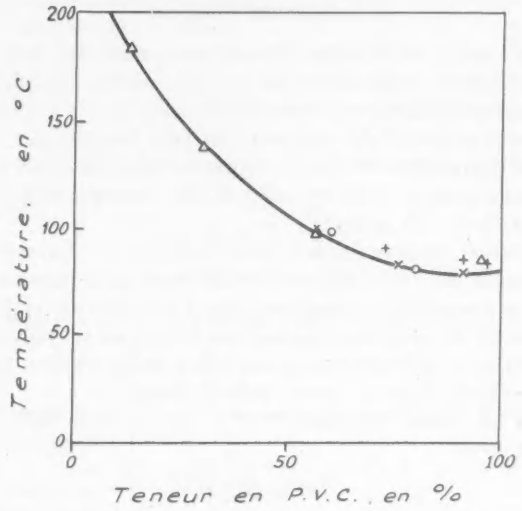


Fig. 3. Copolymères greffés: styrolène-anhydride maléique surpolychlorure de vinyle à differents teneurs en ozonides: (+) 0,15 × 10^{-4} mole/g de polymère; (×) 0,37 × 10^{-4} mole/g; (△) 0,74 × 10^{-4} mole/g; (○) 1,18 × 10^{-4} mole/g. Température de module 10 kg/mm.²

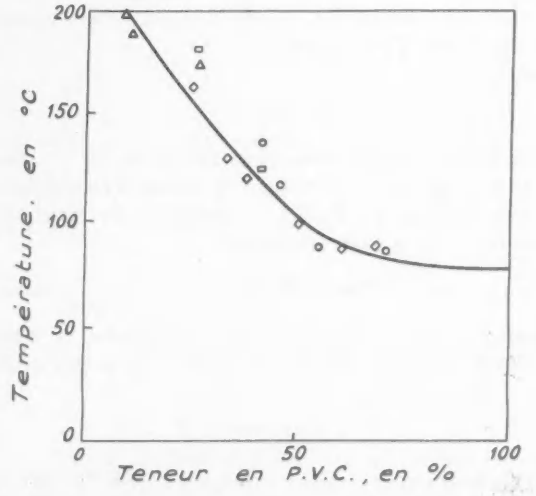


Fig. 4. Copolymères greffés: chlorure de vinyle sur copolymère styrolène–anhydride maléique à differents teneurs en ozonides: (△) 1 × 10^{-4} mole/g de polymère: (□) 2,5 × 10^{-4} mole/g: (○) 5,2 × 10^{-4} mole/g; (◇) 1 × 10^{-3} mole/g. Température de module 10 kg/mm².

L'Ecoulement Visqueux

Pour cette mesure, on étudie la vitesse d'écoulement du produit à travers une filière circulaire située à la base d'un piston creux appliqué sur une masse de polymère enfermé dans un cylindre.

Pour éviter d'atteindre des températures trop élevées qui risquaient de provoquer la dégradation du polychlorure de vinyle, il a fallu utiliser des filières de fortes sections (diamètre de 5, 6, 8 et 10 mm) et une pression appliquée assez élevée (60 kg/cm²).

La température est augmentée linéairement avec le temps (0,7 °C/min), et l'enfoncement du piston qui est proportionnel à la masse écoulée voit son mouvement amplifié et enregistré grâce à une adaptation d'un système déjà décrit et utilisé pour des études dilatométriques sur polymères.[6]

On obtient ainsi des courbes de variation de la fraction de polymère écoulée à travers la filière, en fonction de la température.

Si l'on a V = vitesse d'écoulement, S = section de la filière, η = viscosité, on peut écrire:

$$V = KS/\eta$$

ou

$$\eta = KS/V$$

pour une température donnée. (K est spécifique de chaque polymère et du système de mesure utilisé.)

En fait, pour toutes les courbes, on observe les polymères à l'instant où l'écoulement devient perceptible. A cet instant, indépendamment de la filière, on a une vitesse d'écoulement v_r.

A ce point, on a

$$\eta = KS/v_r$$

Si on utilise les différentes filières de section S_1, S_2, S_3, ..., on mesure les températures pour lesquelles on obtient la vitesse d'écoulement v_r et on a différentes températures T_1, T_2, T_3, et auxquelles les copolymères greffés ont les viscosités η_1, η_2, η_3, pour lesquelles

$$\eta_1 = K\,S/v_r$$

La viscosité du polymère varie avec la température et on admet couramment pour l'évolution de la viscosité en fonction de la température, une loi du type

$$\eta = Ae^{-E/RT}$$

où A est un facteur qui caractérise le polymère et E l'énergie d'activation de la viscosité.

En fait, le domaine d'étude de l'énergie d'activation de l'écoulement visqueux n'est valable que dans un domaine de température où la viscosité est inférieure à 10^1 poises.[12,13,14a]

Dans le cadre de cette étude, E peut être calculé en comparant η obtenu pour deux températures voisines.

Dans le cadre de cette étude, pour mesurer E on utilise deux filières de sections différentes et on mesure les températures auxquelles le produit atteint la même vitesse d'écoulement pour les deux filières de section S_1 et S_2.

Le produit a alors aux deux températures obtenues T_1 et T_2 deux écoulements visqueux η_1 et η_2 et l'on a

$$\eta_1 = (K/v_r)S_1 = Ae^{-E/RT_1}$$

et

$$\eta_2 = (K/v_r)S_2 = Ae^{-E/RT_2}$$

l'énergie d'activation de l'écoulement visqueux s'obteient en écrivant

$$\eta_1/\eta_2 = S_1/S_2 = e^{-E/RT_1}/e^{-E/RT_2}$$

Dans cette égalité S_1, S_2, T_1, et T_2 sont mesurables, et E peut donc être déterminé facilement.

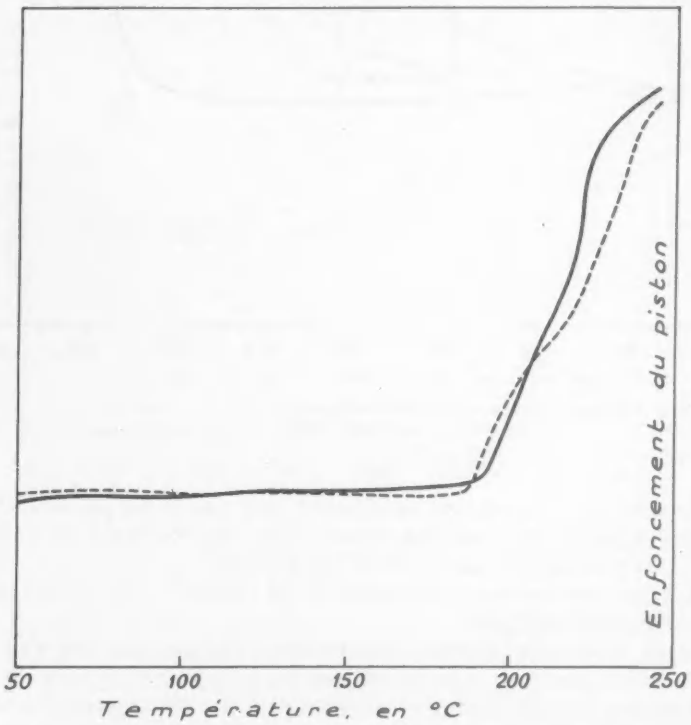


Fig. 5. Ecoulement visqueux de deux copolymères greffés identiques en composition et en ozonisation: (——) 9,17% PVC; (- -) 9,50% PVC.

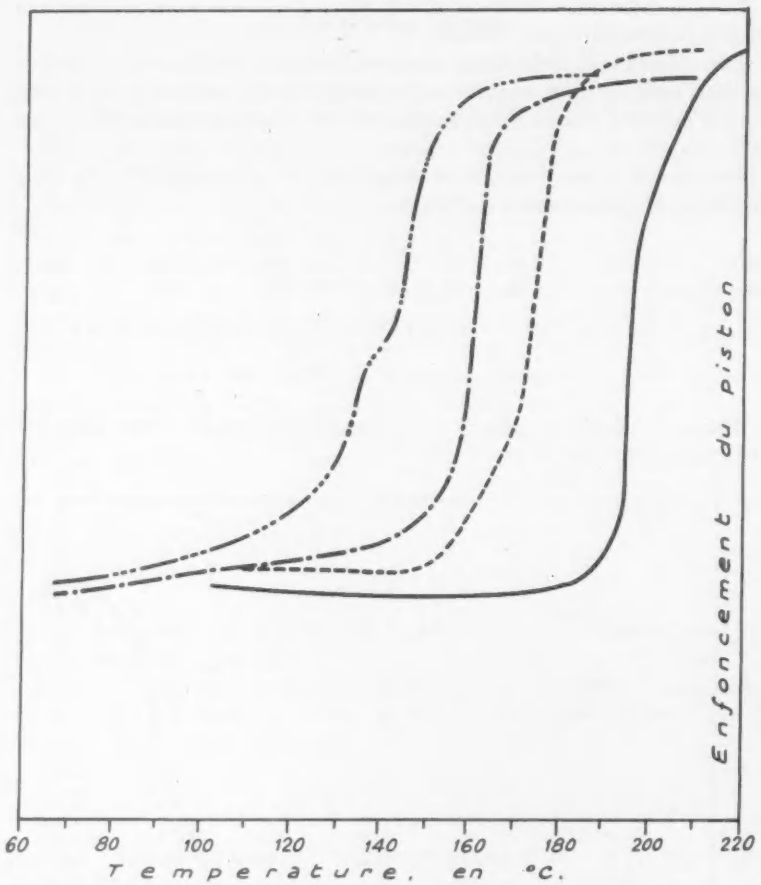


Fig. 6. Greffage styrolène–anhydride maléique sur PVC: (–·–·–) 95% PVC; (–·–) 78% PVC; (----) 56,5% PVC; (——) 30% PVC. Teneur en ozonides 0,74 × 10^{-4} mole/g.

La méthode de mesure est reproductible avec une bonne précision et la Figure 5 montre deux courbes obtenues avec la même filière pour deux produits pratiquement identiques en composition.

Les deux courbes sont superposées, ce qui prouve la reproductibilité et la validité de la méthode.

Si on examine les courbes d'écoulement visqueux pour une série de copolymères greffés de styrolène–anhydride maléique sur polychlorure de vinyle, pour une série homogène en ozonisation et variable en composition, on obtient les résultats rassemblés sur la Figure 6 qui montrent que l'écoulement démarre à une température d'autant plus élevée que le produit est riche en styrolène–anhydride maléique.

Dans le cas d'une série parallèle également homogène en ozonisation, variable en composition, mais de sens de greffage inversé, on obtient des résultats semblables (Fig. 7). C'est-à-dire que la fluidité est diminuée par une augmentation de la teneur en styrolène–anhydride maléique.

Si dans chaque série correspondant à un sens de greffage on examine deux produits de même composition pondérale, mais de taux d'ozonisation

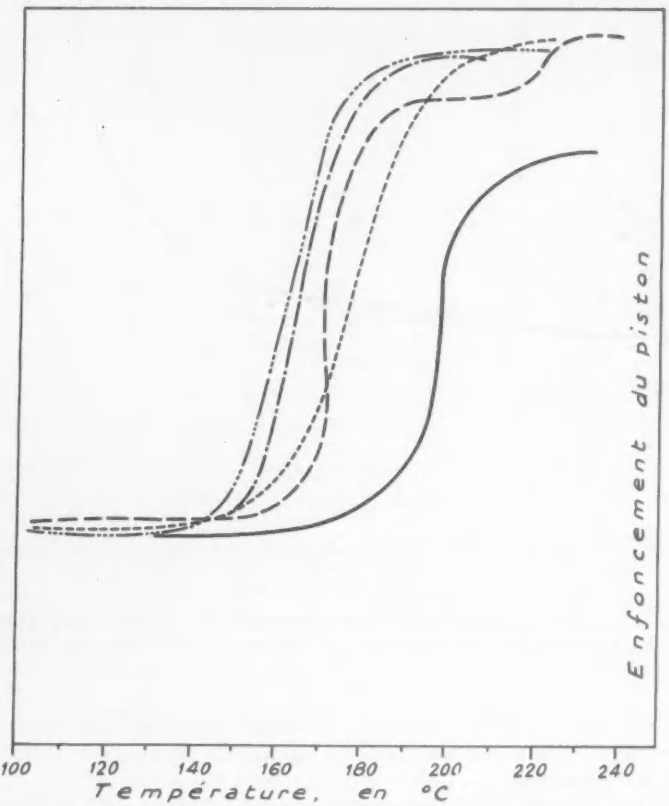


Fig. 7. Greffage chlorure de vinyle sur copolymere styrolène–anhydride maléique: (–···–) 67% PVC; (–·–) 59% PVC; (––) 34% PVC; (- -) 38% PVC; (——) 17% PVC. Teneur en ozonides 9×10^{-4} mole/g.

très différents, on peut voir (Fig. 8) que les copolymères greffés sont d'autant plus visqueux que le taux d'ozonisation est plus faible, c'est-à-dire d'autant plus visqueux que les greffons latéraux sont longs.

Dans le Tableau III et sur la Figure 9 sont rassemblés les résultats obtenus pour la température correspondant à la vitesse d'écoulement v_r.

Ces résultats correspondent à des produits variables en composition, en sens de greffage et en taux d'ozonisation.

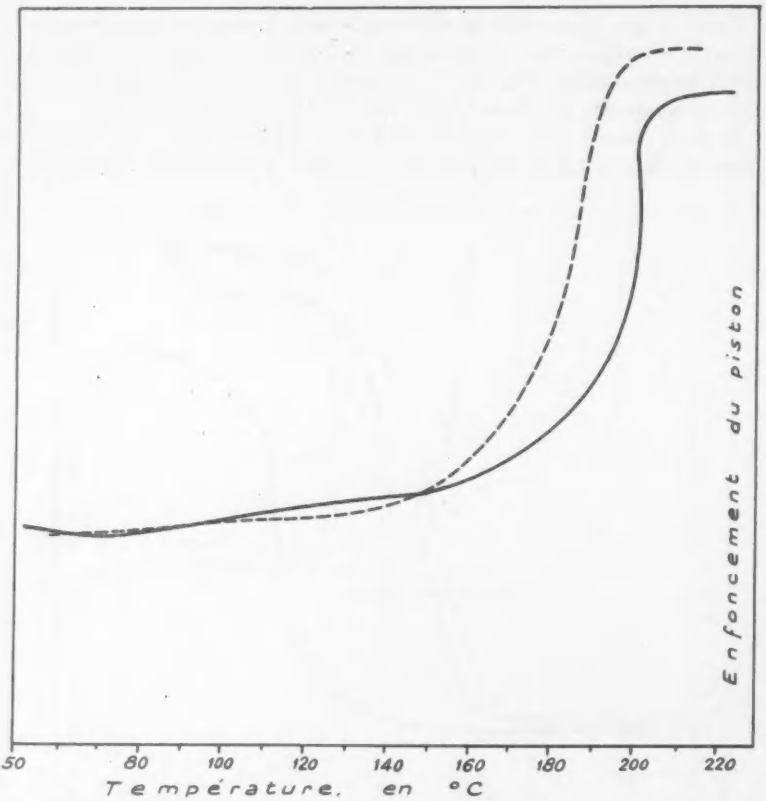


Fig. 8. Greffage styrolène–anhydride maléique sur PVC: (--) teneur en PVC 78,5%, teneur en ozonides 0.74×10^{-4} mole/g; (——) teneur en PVC 73%, teneur en ozonides $0{,}15 \times 10^{-4}$ mole/g.

Si au lieu d'examiner la viscosité on examine l'énergie d'activation de la viscosité, on obtient des résultats plus significatifs parce que les différences sont beaucoup plus marquées.

Dans le Tableau IV sont rassemblés les résultats obtenus sur les différents copolymères greffés.

Les différences sont nettes puisque les valeurs trouvées varient entre 9 kcal. pour le polychlorure de vinyle et 133 kcal. pour le copolymère styrolène–anhydride maléique.

Pour les copolymères greffés de styrolène-anhydride maléique sur polychlorure de vinyle, on voit (Tableau IV et Fig. 10) que l'énergie d'activation croît régulièrement avec la teneur en styrolène–anhydride maléique.

Pour les copolymères greffés inverses, le sens d'évolution est le même. (Tableau IV of Fig. 10) E croît avec la teneur en styrolène–anhydride maléique.

TABLEAU III

Valeurs de la Température Correspondant à v_r avec une Filière de 6 mm

Greffage styrolène–anhydride maléique sur polychlorure de vinyle			Greffage chlorure de vinyle sur copolymère styrolène–anhydride maléique		
Teneur en ozonides, mole $\times 10^{-4}$/g de polymère	Teneur en chlorure de vinyle, %	Température de vitesse d'écoulement $v\eta$, °C.	Teneur en ozonides, mole $\times 10^{-4}$/g de polymère	Teneur en chlorure de vinyle, %	Température de vitesse d'écoulement $v\eta$, °C
0,15	73	173	1	8,2	198
	91	179		9,2	188
	97	160		23	174
0,37	57	163	2,5	25	192
	76	167		40	187
	91	153		49	182
0,74	13	107	5	44	175
	30	186		54	172
	56	171		69	160
	78	167			
	95	152	10	17	194
				33,5	172
				38	168
1,18	60	165		59	159
	79	169		67	154
	91	148			
			Mélanges A		
			B	50	160
			C		

TABLEAU IV

Energie d'Activation de la Viscosité

Greffage styrolène–anhydride maléique sur polychlorure de vinyle			Greffage chlorure de vinyle sur copolymère styrolène–anhydride maléique		
Teneur en ozonides, mole $\times 10^{-4}$/g de polymère	Teneur en Chlorure de vinyle, %	Energie d'activation, kcal/mole	Teneur en ozonides, mole $\times 10^{-4}$/g de polymère	Teneur en Chlorure de vinyle, %	Energie d'activation, kcal/mole
0,15	73	12	2,5	40	15
	91	8		49	19
0,37	57	15	5	44	27
	76	16		54	21
	91	10			
			10	17	61
0,74	13	41.5		33,5	34,5
	30	27		38	37,5
	56	13,7		59	22
	78	11,5		67	19,5
	95	10,5			
			Copolymère		
1,18	60	40	styrolène–	1	133
	79	26	anhydride		
	91	18	maléique		
	Polychlorure de vinyle	9			

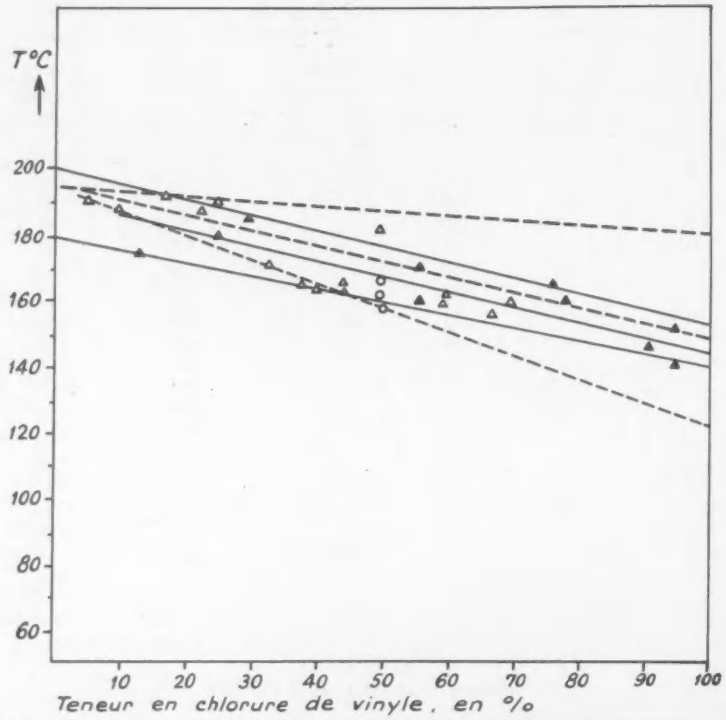


Fig. 9. Température d'écoulement de vitesse V_η: (△) série A, chlorure de vinyle sur styrolène–anhydride meléique; (▲) série B, styrolène–anhydride maléique sur PVC; (O) mélanges; (- -) faisceau de la serie A et bissectrice; (- -) faisceau de la série B et bis sectrice.

Sur la Figure 11 sont montrés les sens d'évolution en fonction du degré d'ozonisation pour plusieurs compositions et pour les deux sens de greffage.

Les résultats obtenus enfin pour les mélanges sont: mélange A, 11 kcal; mélange B 14 kcal; mélange C 25 kcal; mélange D 9 kcal.

DISCUSSION DES RESULTATS

La Module de Torsion

Si l'on examine chacune des Figures 3 et 4, on voit que la température correspondant approximativement au point de transition de second ordre varie avec la composition et est d'autant plus élevée que la teneur en styrolène–anhydride maléique est plus élevée.

Sur la Figure 3 en examinant la série voisine de 75% de chlorure de vinyle en composition, on constate que la température est légèrement plus élevée si le taux d'ozonisation est plus faible c'est-à-dire si la longueur des greffons est plus grande.

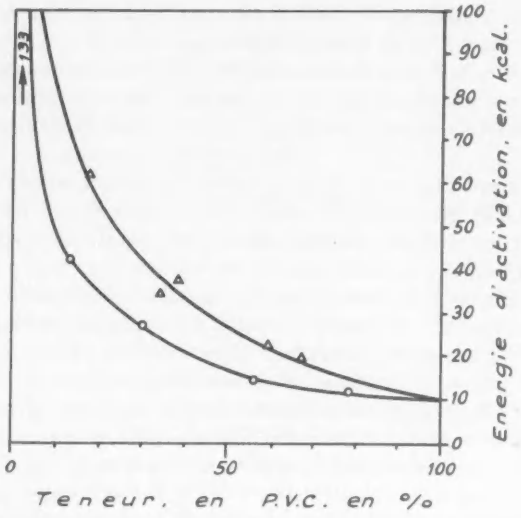


Fig. 10. Energie d'activation de l'écoulement visquex: (O) styrolène–anhydride maléique sur PVC, teneur en ozonides $0,7 \times 10^{-4}$ mole/g; (Δ) chlorure de vinyle sur copolymère styrolène–anhydride maléique teneur en ozonides 1×10^{-3} mole/g.

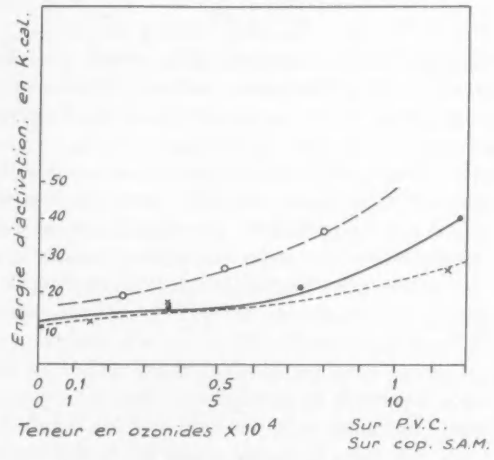


Fig. 11. Energie d'activation de l'écoulement visqueux: (●) greffage styrolène—anhydride maléique sur PVC, teneur en PVC 55–60%; (×) greffage styrolène–anhydride maléique sur PVC, teneur en PVC 75–80%; (O) greffage chlorure de vinyle sur copolymère styrolène–anhydride maléique, teneur en PVC 35–40%.

Cette même remarque est valable pour la Figure 4, pour les produits contenant environ 25% de chlorure de vinyle.

Si on essaye de comparer les deux courbes 3 et 4 qui correspondent à des sens de greffage différents, on constate que ces deux courbes se superposent à peu près exactement, ce qui indique que le sens de greffage est sans influence.

En fait, on sait que le point de transition de second ordre est d'autant plus élevé que les groupements latéraux sont rigides et qu'il est également plus élevé si les groupements latéraux permettent le développement de forces de. Van der Waals intenses.[14c]

Les deux raisons sont rassemblées dans le cas du copolymère styrolène–anhydride maléique. Plusieurs facteurs peuvent influencer, dans des sens différents, l'énergie d'activation de la viscosité. C'est ainsi que les copolymères greffés intermédiaires en composition entre le polychlorure de vinyle et le copolymère styrolène–anhydride maléique offrent normalement des valeurs intermédiaires entre les deux polymères puisque la mobilité d'ensemble de la macromolécule obtenue sera la moyenne des mobilités des segments cinétiques constitutifs.[1,14c]

Par ailleurs, il faut considérer que dans ces copolymères greffés, des groupements latéraux plus longs doivent être responsables d'enchevêtrements plus nombreux qui conduisent à une viscosité plus grande pour une température donnée que si ce copolymère a des greffons courts.

Or, le point de transition de second ordre se situe environ dans un domaine où la viscosité à une valeur de 10^{11} à 10^{12} poises.[15]

Comme la viscosité obéit à une loi du type

$$\eta = KN^*$$

où N^* est la masse moléculaire apparente du polymère, c'est-à-dire que N^* est une valeur qui comprend la masse moléculaire vraie augmentée des enchevêtrements possibles. On peut penser que le point de transition sera plus élevé pour des greffons latéraux plus longs.

Dans le système de copolymères greffés étudié ici, à savoir le chlorure de vinyle d'une part, et copolymère styrolène–anhydride maléique d'autre part, on a bien observé une différence pour des produits à greffons plus longs mais cette différence est moins marquée que celle que l'on a pu observer pour des copolymères greffés de styrolène et d'acrylonitrile.

Le sens de greffage n'apporte pas d'influence majeure, mais lorsque les molécules sont à l'état condensé, les différentes branches étant enchevêtrées les unes dans les autres, avec une densité d'enchevêtrement grande, la différence entre tronc et greffons ne peut plus être marquée.

Elle peut l'être par contre pour des greffons trop courts pour pouvoir s'enchevêtrer. En fait dans le couple choisi ici, la différence n'apparaît pas.

Si on examine le cas des mélanges, les deux polymères n'étant pas compatibles, les chaînes de l'un ne peuvent être ni enchevêtrées ni associées aux chaînes de l'autre, ce qui explique que la valeur trouvée pour le point

de transition soit celle du corps le moins visqueux, c'est-à-dire le polychlorure de vinyle comme on le voit avec les mélanges A, B, C, et D.

Par contre dans le cas des mélanges ou par un artifice, on arrive à disperser plus finement les constituants de l'un parmi les constituants de l'autre, comme c'est le cas du mélange E la valeur trouvée est proche de celle obtenue avec les copolymères greffés.

L'Ecoulement Visqueux

Si on accepte le fait que le point de transition de second ordre apparent correspond à une viscosité donnée, la viscosité à une température donnée doit évoluer dans le même sens que le point de transition de second ordre en fonction de la composition du taux d'ozonisation et du sens de greffage.

Toutefois, en fonction de l'énergie d'activation de la viscosité, les valeurs relatives des viscosités de deux produits à deux températures différentes peuvent être inversées aussi vaut-il mieux discuter avant tout de l'énergie d'activation de la viscosité ce qui permettra ensuite une meilleure interprétation de la valeur de l'écoulement visqueux d'un copolymère greffé donné à une température donnée.

L'énergie d'activation de la viscosité sera une fonction des forces intermoléculaires et de la rigidité conférée par les groupes latéraux.

La vitesse d'écoulement des molécules est régie par la fréquence de déplacement (jumps frequency) des segments dans la macromolécule, soit φ cette valeur.

Si on considère maintenant une macromolécule greffée, ayant un grand nombre de greffons courts dotés d'une liberté de mouvement, on peut penser que la valeur moyenne de φ sera accrue par rapport à ce qu'elle serait pour une molécule greffée ayant des greffons très longs.

Par ailleurs, dans un ensemble de molécules greffées de même composition globale mais à greffons de plus en plus longs (ou de plus en plus espacés) il y aura un niveau[14c] où les greffons seront assez longs pour s'enchevêtrer.

Or cet enchevêtrement, fonction de la masse moléculaire et de la densité en molécules de polymère, ne varie guère avec la température.[14a]

Donc dans ce dernier cas, l'influence de la température sur la facilité de mouvement, donc sur l'écoulement visqueux, sera réduite par rapport à ce qu'elle est pour des greffons plus courts non enchevêtrés.

Donc l'énergie d'activation de l'écoulement visqueux sera plus faible pour des greffons longs enchevêtrés que pour des greffons courts non enchevêtrés.

Les forces d'attraction intermoléculaire sont en partie régies par la composition et on observe bien que l'énergie d'activation est d'autant plus élevée que le copolymère greffé est plus riche en styrolène–anhydride maléique.

En fait, on observe que pour une composition donnée, l'énergie d'activation est d'autant plus élevée qu'il y a beaucoup de petits chaînons latéraux courts, c'est-à-dire lorsque les copolymères greffés sont préparés à partir d'un taux d'ozonisation plus élevé.

Dans un copolymère greffé à l'état d'équilibre, les chaînons de l'un des éléments sont liés aux chaînons de l'autre élément. L'ensemble des macromolécules est en outre enchevêtré et le sens de greffage ne peut plus apporter de caractéristique particulière à cet ensemble enchevêtré et lié, et le sens de greffage ne peut guère, dans les cas moyens, se manifester par une différence de comportement rhéologique.

Toutefois le sens dans lequel le greffage est effectué peut permettre de modifier le rapport de longueur des éléments A et B constitutifs du copolymère greffé et dans ce cas, ce rapport de longueurs modifie les caractéristiques du produit.

Si maintenant, on examine l'évolution de la viscosité en partant du point de transition de second ordre, on constate expérimentalement qu'à ce niveau elle est surtout une fonction de la composition et croissante avec la teneur en styrolène–anhydride maléique.

Partant de là, l'évolution de la viscosité sera une fonction de l'énergie d'activation.

Considérons deux copolymères greffés A et B dont un produit A sensiblement plus riche en styrolène–anhydride maléique, on aura pour le point de transition de second ordre

$$T_g \text{ A} > T_g \text{ B}$$

donc si l'on considère les viscosités à l'une de ces températures, on aura à T_g A

$$\eta_A > \eta_B$$

Mais si A a des greffons très courts et si B a des greffons très longs, on aura des énergies d'activation de viscosité telles que $E_A \gg E_B$ donc en fonction de la température, la viscosité de A décroîtra plus vite que celle de B, ce qui fait que, à une température très supérieure à T_g, et notamment à la température correspondant à l'écoulement à travers une filière, soit T_gA la viscosité de A peut être inférieure à la viscosité de B et on a alors $\eta_A > \eta_B$ à T_gA, mais ηA $< \eta$B à v_rA ou encore T_gA $> T_g$B, T_{v_r}A $< T_{v_r}$B pour deux produits de composition à peu près identiques.

Ceci se retrouve en comparant sur les Tableaux III et IV, les deux copolymères A et B greffés sur copolymère styrolène anhydride maléique et caractérisés par A: teneur en ozonides au départ $2 \times 5 \times 10^{-4}$ mole/g, teneur en styrolène–anhydride maléique 60%; B: teneur en ozonides au départ 5×10^{-4} mole/g., teneur en styrolène–anhydride maléique 56%. On a donc:

$$T_g\text{A} = 125\,°\text{C} > T_g\text{B} = 118\,°\text{C}$$

Or, on trouve pour filière de 8 mm

$$T_v\text{A} = 176\,°\text{C} < T_v\text{B} = 181\,°\text{C}$$

Berlin et ses collaborateurs[3] étaient arrivés à la conclusion que le sens de greffage était important pour la fluidité du copolymère greffé dans le

système polychlorure de vinyle polyméthacrylate de butyle, or leur conclusion n'est basée que sur quelques expériences où l'influence de l'écartement des greffons n'a pas été étudiée et il est possible que les grandes différences observées entre deux copolymères de même composition et de sens de greffage inversé soient dues à des rapports de longueurs des chaînes des greffons et des troncs très différents.

Un autre facteur dans le calcul de l'énergie d'activation de la viscosité est à prendre en considération, c'est le domaine de température dans lequel la mesure est effectuée puisque cette énergie d'activation varie beaucoup autour du point de transition de second ordre T_g pour passer par un maximum à T_g. En fait, l'énergie d'activation a été mesurée à environ 100 °C au dessus de T_g sauf pour les produits très riches en styrolène–anhydride maléique où l'écart entre la température de mesure était faible.

Toutefois, les mesures ont été effectuées à des températures inférieures à celles utilisées par d'autres auteurs[14b,16] et peuvent expliquer les valeurs élevées trouvées comparativement a d'autres méthodes puisque nous avons trouvé 23 kcal pour le polyéthylène entre 115° et 125 °C et 45 kcal pour le polystyrène entre 120° à 130 °C.

Si on examine le cas des mélanges, on se trouve dans le cas de polymères de très longues chaînes où les intéractions entre chaînes de composition différentes sont négligeables par suite de la tendance à la démixion, donc toutes circonstances pour avoir une énergie d'activation très faible. C'est bien en réalité ce que l'on observe, ce qui fait que si les valeurs de T_g sont faibles par rapport à celles des copolymères greffés, étant données les valeurs faibles de E, la viscosité diminue peu avec la température et on se retrouve avec une valeur relativement élevée de T_r.

CONCLUSION

Dans un système de copolymères greffés composé d'une part de chlorure de vinyle et d'autre part de styrolène et d'anhydride maléique, plusieurs caractéristiques sont à considérer: la composition chimique; l'écartement et la longueur des greffons; le sens de greffage.

Il s'avère que le point de transition de second ordre mesuré par variation du module de torsion croît avec la teneur en styrolène–anhydride maléique et se situe entre 80 °C et 200 °C.

Il est plus élevé si les greffons sont plus écartés donc plus longs à composition égale.

Il est indépendant du sens de greffage.

L'énergie d'activation de l'écoulement visqueux qui est accrue par les forces intermoléculaires et par la mobilité des segments, croît avec la teneur en styrolène–anhydride maléique.

Elle est beaucoup plus élevée à composition égale si les greffons sont courts et nombreux.

Les mélanges préparés à partir des mêmes produits ont un point de transition de second ordere identique à celui obtenu pour le polychlorure de

vinyle sauf ceux préparés par mélange d'un latex de polychlorure de vinyle et d'une solution aqueuse ammoniacale du copolymère 1:1 styrolène–anhydride maléique. Dans ce dernier cas, le point de transition est équivalent à ceux des copolymères greffés de même composition.

L'énergie d'activation de la viscosité des mélanges évolue à composition donnée, entre celle obtenue pour le polychlorure de vinyle et celle du copolymère greffé de composition identique à celle du mélange et de greffons très longs.

Les auteurs remercient Madame Morvezen qui a collaboré à la préparation des copolymères greffés et à l'étude de leurs comportements rhéologiques et Monsieur Famechon qui a collaboré à l'étude des mélanges ainsi que la Société Kléber-Colombes qui autorise la publication de ces résultats.

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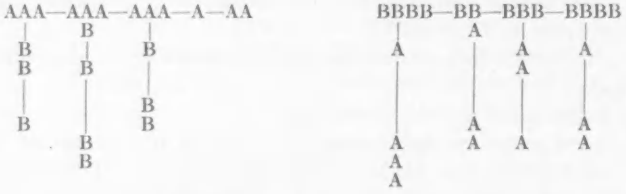
Résumé

Lorsque l'on considère un copolymère greffé, on a affaire à un produit qui contient des chaînes longues des deux éléments, ces chaînes étant liées entre elles, selon l'un des deux schémas suivants:

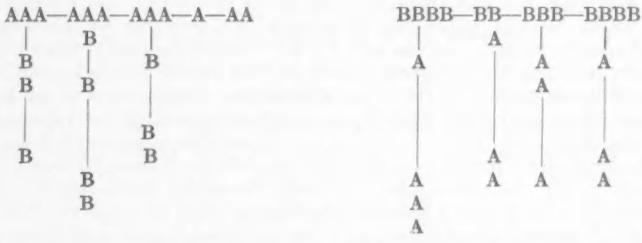


Chacun de ces deux types de chaînes doit influencer le comportement de l'autre. Le but de cette étude est de voir quelle est l'influence mutuelle des deux éléments constitutifs d'un copolymère greffé. Les deux élements constitutifs sont le chlorure de vinyle d'une part et le système 1:1 styrolène–anhydride maléique d'autre part. L'étude est complétée par celle des mélanges de deux polymères de base, ces mélanges étant préparés par

plusieurs techniques différentes. Les propriétés prises en considération sont le point de transition de second ordre mesuré par variation du module de rigidité d'une part et l'écoulement à l'état fondu ainsi que la variation de cet écoulement avec la température. On examine l'influence des taux de greffage, l'influence de l'écartement des greffons et également l'influence du sens des greffages c'est-à-dire que l'on examine aussi bien les copolymères greffés de styrolène–anhydride maléique sur polychlorure de vinyle et les copolymères greffés de chlorure de vinyle sur copolymère de styrolène et anhydride maléique. Dans ce système particulier, on observe que le point de transition de second ordre est fonction de la composition, il est plus élevé pour des greffons longs et il est indépendant du sens de greffage. On observe en outre que la viscosité à l'état fondu, d'un copolymère à une température donnée varie dans lemême sens, c'est-à-dire qu'elle est fonction de la composition, elle est plus élevée pour des copolymères à greffons longs et elle est sensiblement indépendante du sens de greffage. La variation de la viscosité avec la température est plus rapide pour des produits riches en styrolène-anhydride maléique et pour une composition donnée elle est plus rapide avec des copolymères à greffons courts. Etant donné l'importance de ce dernier facteur, il n'est pas possible de déterminer l'influence particulière du sens de greffage car il faudrait avoir pour chaque sens de greffage représenté sur les deux schémas des copolymères inverses à écartement de greffons identiques. Les résultats obtenus avec les mélanges de A_n et B_n varient avec la technique de mélange utilisé. Dans le cas où l'on a pu réaliser des dispersions extrêment fines de l'un dans l'autre, on a pu obtenir des caractéristiques avoisinant celles des copolymères greffés.

Synopsis

In the study of graft copolymer, two types of linking of the chain sequences can be considered, namely:

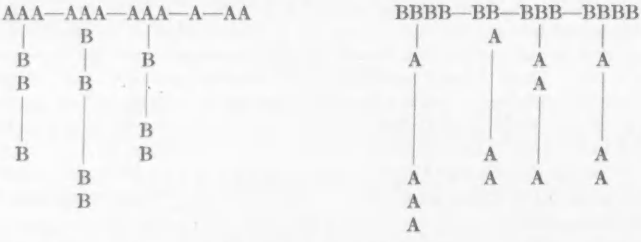


Each type of chain must influence the behavior of the other. In the present paper the mutual influence of both components of the graft copolymer will be studied. Both components are vinyl chloride on one side, and the system 1/1 styrene–maleic anhydride on the other side. The study was completed by the study of mixtures of both polymers, these mixtures being prepared with different techniques. The properties which were examined are the glass transitions point, as measured by the changes of the rigidity modulus, and the melt flow, and the variation of this melt flow with temperature. The influence of the degree of grafting and of the distance between the grafts as well as the influence of the way of grasting (i.e., grafting of styrolene–maleic anhyd.ide into PVC and grafting of vinylchloride on styrene-maleic anhydride copolymers) have been examined. In this system, the second order transition point is a function of the composition; it is higher for long side grafts, and is independent of the way of grafting. Moreover, the melt viscosity ot a copolymer at a given temperature varies in the same direction, i.e., it is a functian of the way of grafting. The chain of viscosity with temperature is more rapid for products with high styrene–maleic anhydride content, and for a given composition it is more rapid for copolymers with short side-grafts. Considering the importance of this last factor, it is impossible to determine the influence of the way

of grafting; indeed for each way of grafting, as represented in the above formula, one should have two copolymers, inverse of each other, with the same distance between side-grafts of an identical length. The results obtained with mixtures of A_n and B_n are different with the technique used for mixing. When extremely fine dispersion of one component in the other was obtained, characteristics obtained were similar to those of graft copolymers.

Zusammenfassung

Bei einem Pfropfcopolymeren hat man es immer mit einem Produkt zu tun, das lange Ketten aus den beiden Elementen enthält, wobei diese Ketten untereinander nach einem der folgenden Schemen verbunden sind:



Jeder dieser beiden Kettentypen beeinflusst das Verhalten des anderen. Das Ziel der vorliegenden Arbeit ist die Ermittlung des wechselseitigen Einflusses der beiden Aufbauelemente eines Pfropfcopolymeren. Die beiden Aufbauelemente sind einerseits Vinylchlorid und andrerseits das 1:1-System Sytrol-Maleinsäureanhydrid. Zur Vervollständigung wird auch eine Untersuchung von Mischeungen der beiden Grundpolymeren durchgeführt, wobei diese Mischungen nach mehreren verschiedenen Verfahren dargestellt werden. Gemessen werden der Umwandlungspunkt zweiter Ordnung mittels der Änderung des Steifigkeitsmodulus und das Fliessen im geschmolzenen Zustand sowie dessen Abhängigkeit von der Temperatur. Untersucht wird der Einfluss des Vernetzungsgrades, der Ausbreitung der Aufpfropfungen sowie des Aufpfropfungssinnes, d.h. dass sowohl Pfropfcopolymere von Styrol-Maleinsäureanhydrid auf Polyvinylchlorid als auch von Vinylchlorid auf dem Styrol-Maleinsäureanhydridcopolymeren untersucht werden. In diesem speziellen System erweist sich der Umwandlungspunkt zweiter Ordnung als Funktion der Zusammensetzung; et ist für lange Aufpfropfungen und von Aufpfropfungssinn unabhängig. Die Schmelzviskosität eines Copolymeren ändert sich bei gegebener Temperatur im gleichen Sinn, d.h. sie ist eine Funktion der Zusammensetzung, liegt für die Copolymeren mit langen Aufpfropfungen höher und ist im wesentlichen von Aufpropfungssinn unanhängig. Die Temperaturabhängigkeit der für Styrol-Maleinsäureanhydrid-reiche Produkte stärker und bei gegebener Zusammensetzung stärker für Copolymere mit kurzen Aufpfropfungen. Wegen der Bedeutung des letzteren Faktors ist es nicht möglich den speziellen Einfluss des Aufpfropfungssinnes zu bestimmen, da man für jeden Aufpfropfungssinn inverse Copolymere mit identischer Aufpfropfungslänge zur Verfügung haben müsste. Die Ergebnisse bei den Mischungen von A_n und B_n hängen von verwendeten Mischungsverfahren ab. In den Fällen, in welchen extrem feine Verteilung des einen im andern erreicht werden konnte, waren die charakteristischen Eigenschaften denjenigen der Pfropfcopolymeren recht ähnlich.

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Reactive Fiber. II. Chemical Reactivities of Cellulose Fiber Grafted with Glycidyl Methacrylate

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INTRODUCTION

Chemical reactivities of the synthetic fiber prepared from the copolymer of acrylonitrile and glycidyl methacrylate have been reported in our first paper on the reactive fibers. In that study, epoxy groups in the fiber were treated with dyes which contain amino or phenolic hydroxyl groups, or reacted with amines and oxyamines or with α-amino acids and amino sulfonic acids.[1] In the course of the study we have found that glycidyl methacrylate (GMA) resembles methyl methacrylate in copolymerization reactivity. We have extended the study to the syntheses of the reactive polymers which contain glycidyl methacrylate instead of methyl methacrylate units. Isotactic polypropylene, polyamides, polyvinyl chloride, and cellulose fibers, all grafted with glycidyl methacrylate, were investigated as reactive fibers. In the present paper chemical reactivities of the cellulose fibers (Bemberg and viscose rayons) grafted with GMA are reported in detail.

Reactive cellulose fiber (fiber II) was prepared by grafting GMA on cellulose analogously to the redox method with ceric salt[2] described for methyl methacrylate. Denier and elastic recovery of fiber II increased with increasing grafting ratio, but strength and elongation decreased. By opening the epoxy rings of the fiber II, the dyes were chemically bonded to the fiber through their amino or phenolic hydroxyl groups. In this case the reactive component is the fiber itself and not the dyes as in the reactive dyes. The idea of reactive fibers was thus introduced. The examination of the cross section of the chemically dyed fibers showed that the grafting by the ceric salt method developed from the outside of the fibers.

Modification of fiber II by α-amino acids and aminosulfonic acids, or amination by amines and oxyamines were carried out, and the reactions of hydrogen sulfide, sodium bisulfate, and thioglycolic acid on fiber II were investigated. The ion exchange fibers which are produced from these reactions are discussed.

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RESULTS AND DISCUSSION

Graft Copolymerization of Glycidyl Methacrylate to Cellulose Fiber

To clarify the mechanism of the redox graft polymerization of cellulose by ceric salts, model experiments were carried out in which styrene was polymerized by primary, secondary, tertiary alcohols, 2,3-butylene glycol and oil-soluble ceric salts. The results are shown in Table I.

TABLE I
Redox Polymerization of Styrene by Ceric Salt and Alcohols at 70°C., Time 9 hr., Oil-Soluble Ceric Salt 15 g./l.

Expt. no.	Alcohol	Yield, %
211	None	Small
118	*tert*-butyl	Small
112	Ethyl	6.2
415	Ethyl	5.7
117	*n*-Octyl	6.0
431	*n*-Octyl	6.1
419	*n*-Butyl	6.8
428	*n*-Butyl	6.7
417	Benzyl	8.7
424	Benzyl	8.0
116	Isopropyl	1.5
418	Isopropyl	2.4
421	Isopropyl	2.1
416	*sec*-Butyl	1.5
422	*sec*-Butyl	1.3
429	α-Phenylethyl	1.4
472	2,3-Butanediol	12.3

The only alcohols which can polymerize styrene by redox reaction with ceric salts are primary alcohols; secondary alcohols can be utilized when they are of the 1,2-glycol type. To ascertain whether polystyrene, which was obtained from the redox polymerization by ethyl alcohol–ceric salts, has one hydroxyl endgroup, the polymer (M.W. 6.4×10^4) was treated with tetramethylene diisocyanate in toluene in the presence of dibutyltin dilaurate–triethylenediamine as a complex catalyst. The treated polystyrene had a molecular weight of 11.6×10^4. Accordingly, the above polystyrene was considered to have an endgroup of the type

$$CH_2\text{—}\underset{\displaystyle OH}{\underset{|}{CH}}\text{—}CH_2\text{—}CH\sim$$

From these results graft polymerization of GMA on cellulose by ceric salts is considered to be initiated by the free radicals either at α-carbon of the primary alcohol or at the carbon atom of 1,2-glycols in the glucose unit.

Next, GMA was graft polymerized on cellulose by redox polymerization with ceric ammonium nitrate. The effects of ceric ion concentration,

grafting temperature, GMA concentration, and hydrogen ion concentration on the polymerization rate were investigated in detail.

Figure 1 shows the content of grafting measured by the weight increase against time and concentration of the ceric ion.

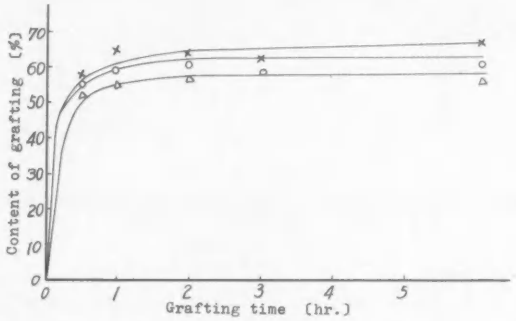
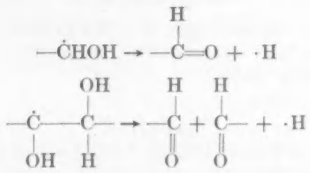


Fig. 1. Relation between GMA concentration and the content of grafting at 30°C.: (○) 0.3×10^{-3} mole/l.; (△) 0.1×10^{-3} mole/l.; (×) 0.6×10^{-3} mole/l.

From the result, oxidative termination by the ceric ion is deduced since the increase of the ceric ion concentration has little effect on the grafting rate.[3]

Figure 2 shows the relation between content of grafting and temperature. The higher the temperature, the smaller is the content of grafting. This tendency can be explained by considering the following reaction mechanism. Free radicals produced by the elimination of hydrogen atoms change to aldehyde rather easily at high temperatures.



The effect of the GMA concentration on the reaction ratio is shown in Figure 3. By choosing a proper ratio of GMA and Bemberg rayon in the polymerization medium, GMA can be grafted without any appreciable loss.

Graft copolymerization in the presence of and without acids clarified the effect of hydrogen ion concentration on the grafting rate. Results of the ring-opening reaction (hydrolysis) in acidic media are given in Table II. The ring-opening ratio of the epoxy group in the GMA-grafted cellulose reached 54% when it is treated under the following conditions: $[Ce^{+4}] = 0.6 \times 10^{-3}$ mole/l.; $[H^+] = 6 \times 10^{-3}$ mole/l., grafting time 1 hr.; temperature 30°C.

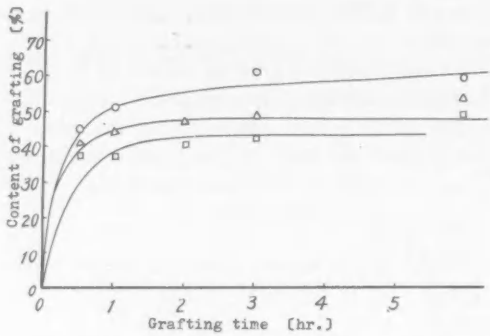


Fig. 2. Relation between the grafting temperature and the content of grafting: (○) 30°C.; (△) 50°C.; (□) 70°C.

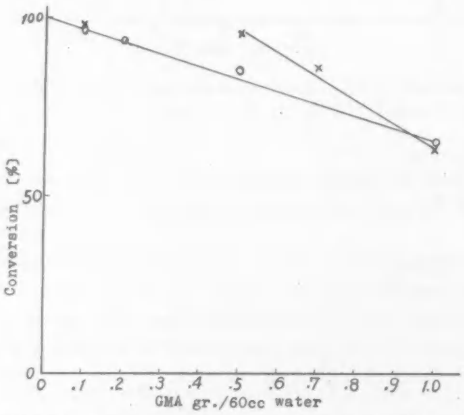


Fig. 3. Effect of H^+ on the conversion of GMA in graft polymerization at 35°C.: (○) no H^+; (×) H^+ present, 1*N* aqueous HNO_3, 0.6 cc./60 cc. water. $[Ce^{+4}] = 0.1N$ aqueous solution, 0.6 cc./60 cc. water.

TABLE II
Ring Opening of Epoxy Group in GMA-Grafted Cellulose Fiber

Extent of grafting, %	Unreacted epoxy group, %	Ring opened epoxy group, %	Degree of ring opening, %	Reaction ratio of epoxy group with amine
44.4	20.45	23.95	54.0	77.4

In Figure 4 is shown the hydrolysis of the GMA in aqueous medium with the presence of nitric acid. In this case hydrolysis of ester was not perceived, but hydrolysis of the epoxy ring occurred rather rapidly.

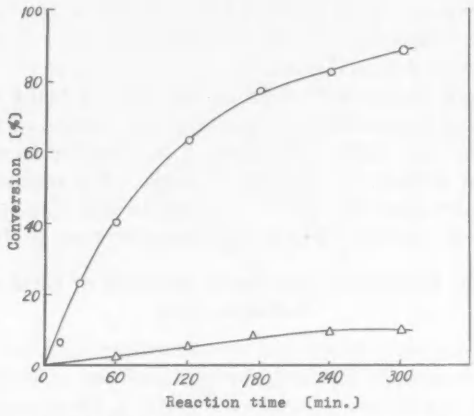
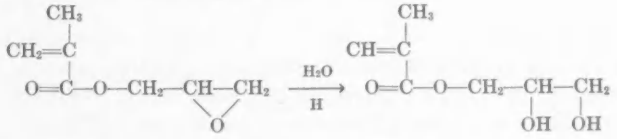


Fig. 4. Hydrolysis of GMA at 35°C.: (O) conversion in the presence of H^+, constant HNO_3 concentration; (Δ) conversion in the absence of H^+.

If hydrolysis occurs, the equation



can be written for the reaction, and a linear relation should be obtained:

$$dx/dt = k_H^0[H^+]W[a - x] = k_H[H^+][a - x] \quad (1)$$

where a is the initial concentration of GMA, x is the reacted amount of GMA, W is the amount of water, and $[H^+]$ is the hydrogen ion concentration mole/l. By transforming eq. (1) we obtain

$$-2.303 \log a/(a - x) = k_H[H^+]t \quad (2)$$

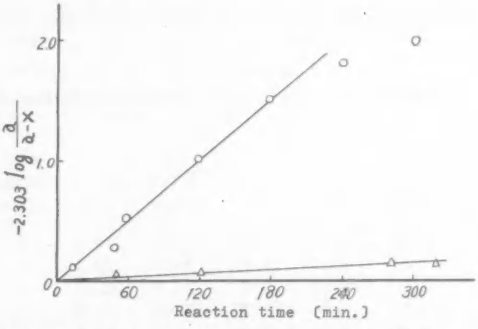


Fig. 5. Hydrolysis of GMA at 35°C.: (O) H^+ present; (Δ) H^+ not present.

Figure 5 verifies eq. (2) and gives a value of 1.398×10^{-4} mole/l. sec. for $k_H[H^+]$. This hydrolysis reaction is considered to occur in monomer or in polymer during the polymerization.

As was already mentioned concerning the effect of GMA concentration, the effect of acid concentration on grafting rate is small at GMA concentrations greater than 1.6%. Therefore, it is advisable to carry the graft polymerization without the presence of acids. The rate of ring-opening hydrolysis is also shown in Figure 5 but practically, ring-opening ratio of the epoxy group remains 5% at a polymerization time of 60 min.

Strength, Elongation, and Elastic Recovery of GMA-Grafted Cellulose Fiber

Strength, elongation, denier, and elastic recovery were measured on three viscose rayon samples of different degrees of grafting. Denier and recovery increased with the increase of content of grafting, but strength and elongation decreased (Figs. 6 and 7, Table III). X-ray analysis of the GMA-

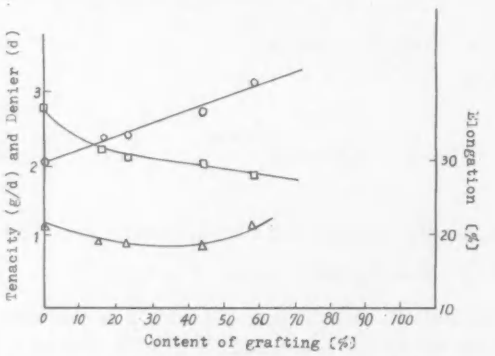


Fig. 6. Mechanical properties of GMA-grafted viscose rayon: (○) denier; (□) tenacity; (△) elongation.

grafted Bemberg rayon showed that the crystallinity and orientation of the fiber does not change before and after the graft polymerization (Fig. 8).

TABLE III
Mechanical Properties of GMA-Grafted Viscose Rayon

No.	Content of grafting, wt.-%	Denier	Strength, g./den. dry	Strength, g./den. wet	Elongation, % dry	Elongation, % wet	Knot strength, g./den.	Knot elongation, %
0	0.0	2.00	2.84	1.80	21.0	23.2	1.72	12.8
1	16.2	2.31	2.23	1.48	19.2	22.1	1.16	9.3
2	23.3	2.40	2.15	1.50	19.0	22.6	1.20	10.2
3	44.4	2.74	2.01	1.39	18.8	24.6	1.23	10.3
4	58.9	3.10	1.81	1.25	21.4	25.1	1.09	10.5

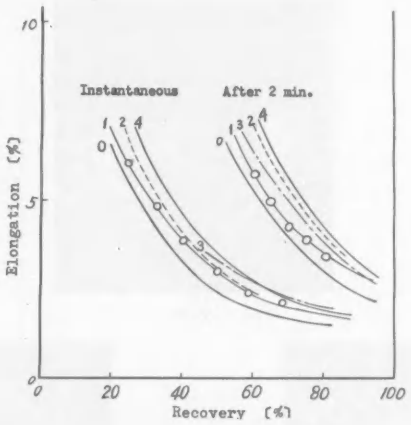


Fig. 7. Elastic recovery of viscose rayon grafted with GMA. The numbers 0, 1, 2, 3, and 4 correspond to the sample numbers in Table III.

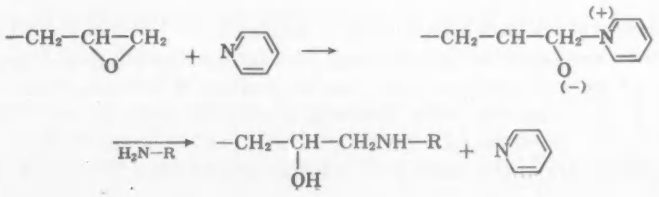
Reaction of Fiber II and Dyes

The epoxy group in fiber II reacts with the amino or phenolic hydroxyl group by opening its ring. Therefore, chemically bonded dyeing can be expected between fiber II and dyes containing an amino or phenolic hydroxyl group. When grafted Bemberg rayon (grafting content 10.5 wt.-%) is treated for 30–60 min. at 60–80°C. in an aqueous dyeing medium which contains Na_2SO_4 and pyridine, it is comparatively easily dyed and the absorbed dyes are not extracted by cyclohexanone and hot water—this fact means the chemically bonded dyeing.

Pyridine here reacts as a catalyst. The catalytic effect of pyridine when Orange II is used as a dye is shown in Figure 9.

Figure 10 shows the effect of the reaction temperature.

The role of pyridine as the catalyst is understood to be formation at a comparatively stable activated complex with the epoxy group; GMA-grafted cellophane, when treated with pyridine, desorbs pyridine on treatment with hot water (90°C.) but not on treatment with cold water; the pyridine in the cellophane can be substituted by amines. These facts and the ultraviolet ray absorption data (Fig. 11) confirm the formation of the activated complex.



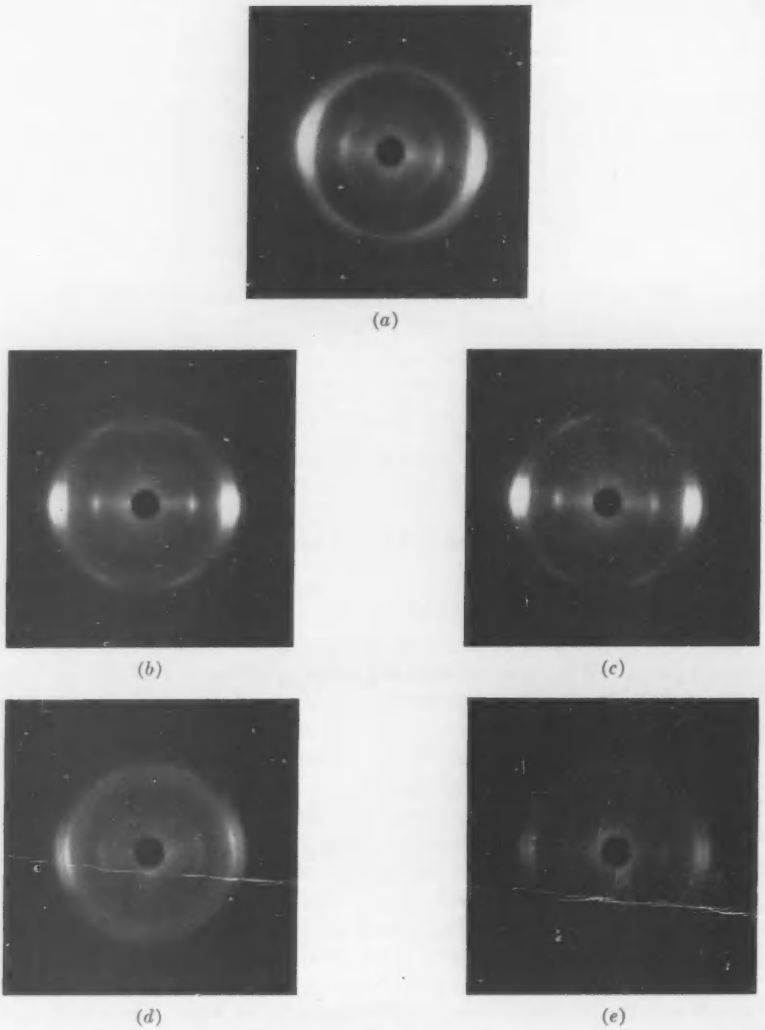


Fig. 8. X-ray diagrams of Bemberg rayon grafted with GMA: (*a*) ungrafted; (*b*) 11.8% grafting; (*c*) 44% grafting; (*d*) 95% grafting; (*e*) 155% grafting.

The dyes which have been bonded to the fiber II are listed in Table IV. The cross section of the fiber II (Fig. 12) after dyeing with Acid Orange II in the presence of pyridine, shows that the grafting of the GMA on cellulose starts from the surface of the fiber and develops into the center when the grafting ratio is increased. On the contrary, grafting starts in the core of the fiber in case of the redox graft polymerization of the Fe^{+2}–H_2O_2–cellu-

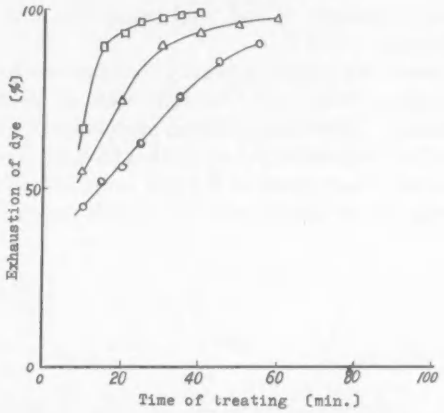


Fig. 9. Effect of pyridine concentration on the reaction of fiber II and acid dye (Acid Orange II) at 50°C. with a ratio of dye/fiber of 0.02:1 and a ratio of media/fiber II of 50:1: (○) 0.2 cc. C_5H_5M/100 cc. media; (△) 0.4 cc./100 cc. media; (□) 0.8 cc./100 cc. media.

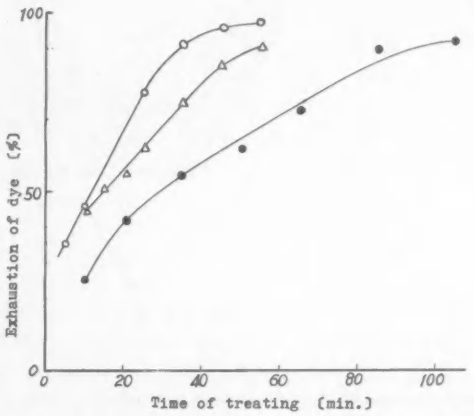


Fig. 10. Effect of temperature on the reaction of fiber II with acid dye (Acid Orange II) in the presence of 0.2 cc. pyridine/100 cc. dye bath at a ratio of dye/fiber of 0.02:1 and a ratio of media/fiber of 50:1: (○) 60°C.; (△) 50°C.; (●) 40°C.

lose system. This fact is only explained by the photographs of the cross section; the details of this investigation will be reported later.

Fastness of the Dyed GMA-Grafted Cellulose to Light and Washing

Viscose rayon cloth (sample 1) was grafted with GMA and was reacted with dyes either in the presence of (sample 4) or without (sample 3) pyridine. Fastness to light and washing was measured on these samples by Fadeometer and Laundrometer. For the comparison, grafted cloth treated

with diethanolamine (sample 5) and wool (sample 2) were also examined. The results are listed in Table V.

From these data it can be said generally that fastness to light decreases while washing fastness increases. This represents an assumption and not yet a final conclusion. In ordinary dyeing, aggregates of dye molecules are formed onto the fiber because of the attraction brought about by hydrogen bonding and van der Waals forces of the dye molecules. In grafted fibers, there is no aggregation of the dye because the dye molecules are dispersed

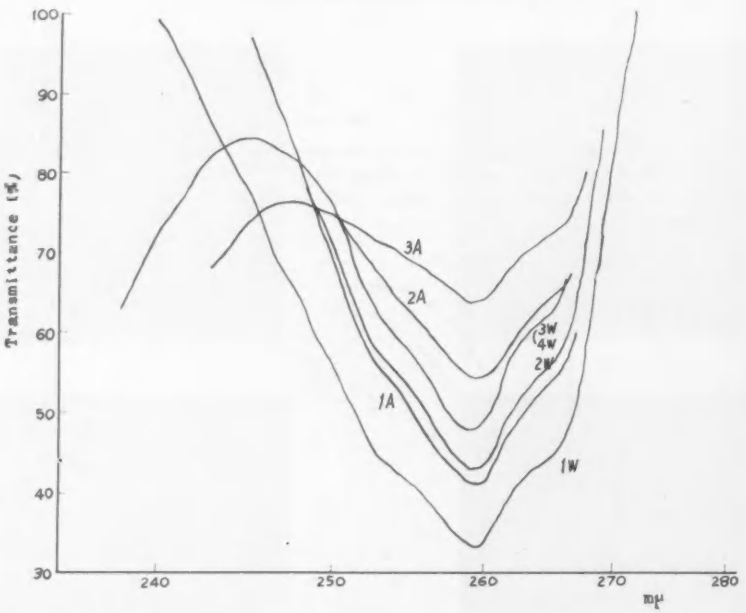
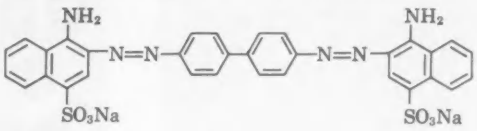
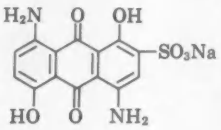
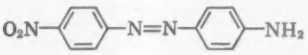
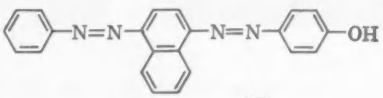
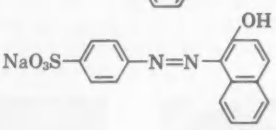
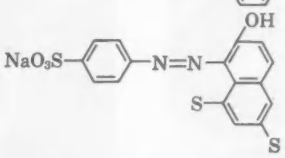


Fig. 11. Ultraviolet spectra of GMA-grafted cellophane treated with pyridine: (*1W*) GMA-grafted cellophane treated with 5% aqueous pyridine solution at 35°C. for 5 min.; (*2W*) after extraction of fiber *1W* with water at 65°C. for 30 min.; (*3W*) after extraction of fiber *1W* with water at 65°C. for 60 min.; (*4W*) after extraction of fiber *1W* with water at 65°C. for 90 min.; (*1A*) GMA-grafted cellophane treated with 5% aqueous pyridine solution at 35°C. for 5 min.; (*2A*) after reaction of fiber *1A* with diethanolamine at 65°C. for 10 min.; (*3A*) after reaction of fiber *1A* with diethanolamine at 65°C. for 30 min.

out of the range of the attractive forces. The reason for this difference is that in ordinary dyeing the mobility of the dye molecule remains, therefore, aggregation results. In grafted fibers, however, this mobility is not present because the dye reacts immediately with the grafted fiber. The aggregates of dye enhance chemical stability to light, therefore the ungrafted fibers have more light stability. But in washing fastness, the re-

TABLE IV

Dye	Structure
Benzopurpurine 4B	
Alizarine Saphirol S.E.	
Dispersol Fast Orange G	
Dispersol Fast Orange B	
Acid Orange II	
Acid Brilliant Scarlet 3R	

acted dye of the grafted fiber cannot be extracted by water, aqueous alkaline solution, or any other ordinary solvent, as may be done when the dye is not reacted with the ungrafted fiber. In this case then, the washing fastness of grafted fibers is superior to ungrafted fibers.

Preparation of Ion Exchange Fibers

Anion exchange fiber and cation exchange fiber were prepared by using the chemical reactivity of GMA-grafted cellulose. The anion-exchange fiber was obtained by the introduction of quaternary ammonium hydroxide and the cation-exchange fiber by introduction of sulfonic, mercapto, and carboxyl groups. The reaction of diethylamine and diethanolamine with GMA-grafted Bemberg rayon (grafting content 100 wt.-%) was examined in anhydrous and aqueous acetone and in water. The results are shown in Figure 13.

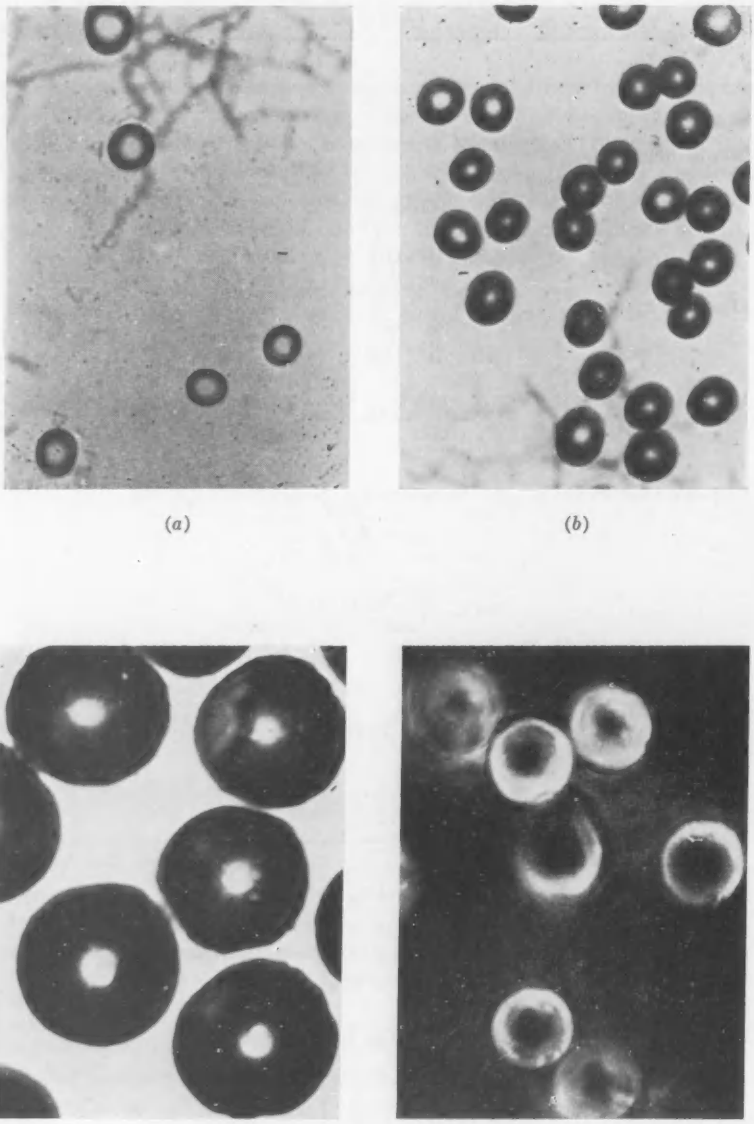


Fig. 12. Cross section of fiber II dyed with Acid Brilliant Scarlet 3R in the presence of pyridine; (*a*) Bemberg rayon grafted with GMA in the presence of ceric salt, 11% grafting; (*b*) Bemberg rayon grafted with GMA in the presence of ceric salt, 25% grafting; (*c*) Bemberg rayon grafted with GMA in the presence of ceric salt, 128% grafting; (*d*) Bemberg rayon grafted with GMA in the presence of H_2O_2–Mohr salt, ca. 5% grafting.

TABLE V
Fastness of the GMA-Grafted Cellulose to Light and Washing

No.	Dye	Fastness[a]	
		Light	Washing
1-1	Benzopurpurine 4B	4	2
1-3		4	3–4
1-4		2	3–4
2-2	Acid Orange II	>5	1
2-3		3	1
2-4		4	2
2-5		3	3
3-2	Acid Brilliant Scarlet 3R	4	1
3-3		—	1
3-4		3–4	3–4
3-5		4	1
4-1	Alizarine Saphirol SE	>5	1
4-2		>5	1
4-3		>5	4
4-4		>5	4
4-5		3	2

[a] The numbers listed in the column labeled fastness indicates the degree of fastness which is classified using numerical values from 1 to 5. The larger the number, the better the fastness. These numbers are approximations determined by visual judgment. Therefore, fastness may be represented by >5 or 3–4.

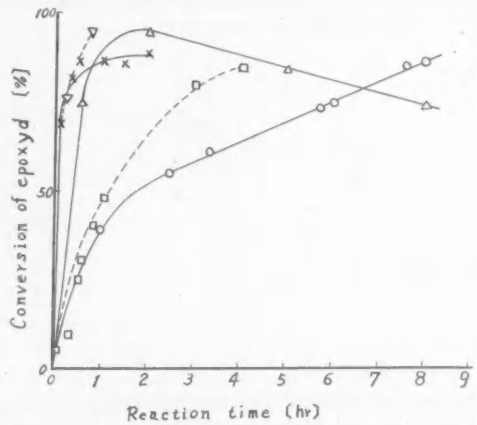
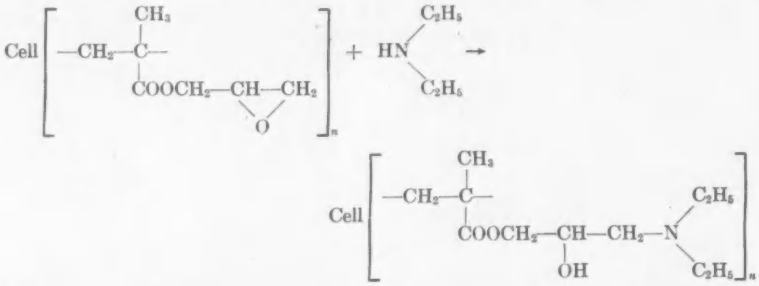


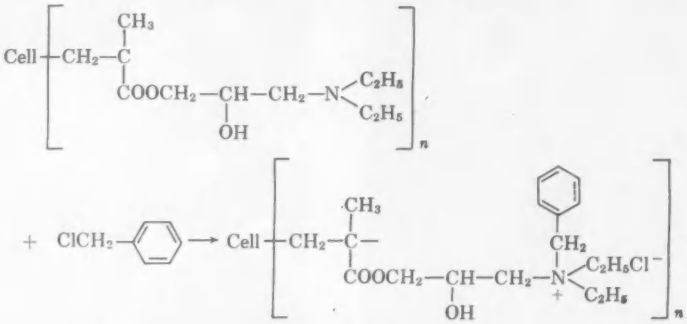
Fig. 13. Effect of reaction medium on amination of fiber II at 65°C.: (○) acetone–diethylamine; (△) acetone–water (20 wt.-% H_2O); (▽) water; (□) water–diethanolamine; (×) water–diethylamine (cograft).

Aqueous acetone gives the highest reaction ratio but it decreases after 2 hr. This is because the reaction rate was measured by the nitrogen content of the products, and hydrolysis of the ester becomes unavoidable.



Water gave the highest reaction rate because cellulose has hydrophilic groups. The reaction of amines was further investigated on Bemberg rayon graft copolymerized with GMA and methyl methacrylate (grafting content GMA 57 wt.-%, MMA 29 wt.-%), but the results were almost the same. On the other hand, the examination of the reaction velocity of MMA–GMA cografted cellulose with amines in homogeneous system showed that GMA homografted cellulose gave the high reaction velocity. This phenomenon was explained by the catalytic reaction of the produced groups. The reason why no difference was observed in the heterogeneous system depends on the fact that the rate-determining step is the diffusion of amines into the cellulose.

Next, quaternary ammonium chloride was prepared in acetone by benzyl chloride on GMA-grafted, diethylamine-treated Bemberg rayon (grafting content 94 wt.-%, N 3.36%, reaction ratio 80%):



The effect of the concentration of the benzyl chloride is shown in Figure 14. The reaction ratio was calculated from the ion exchange abilities. To examine the effect of the dielectric constants of the solvents, acetone, DMF, nitrobenzene, and benzene were used (Table VI). Among them DMF showed the highest reaction ratio, but the dependence of dielectric constant was not practically observed.

Quaternary ammonium salt formation of grafted Bemberg rayon in 50 wt.-% DMF solution of benzyl chloride was carried out at 40, 50, and 65°C. (Fig. 15). The reaction ratio increases with the increasing temper-

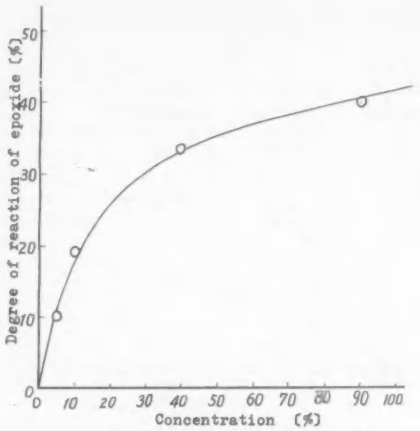
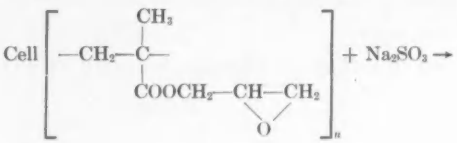
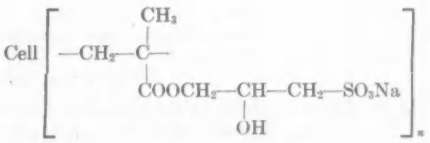


Fig. 14. Degree of reaction of aminated fiber II with benzyl chloride of various concentrations in acetone at 65°C. in 5 hr.

ature, but remains 70% at 65°C. and 6 hr. The reaction in the DMF–water system gave a reaction ratio of more than 90% in 3 hr. at 65°C. because of the hydrophilic nature of the grafted cellulose (Fig. 16).

It is well known that sodium oxysulfonate is produced by the ring-opening addition reaction of epoxy group and Na_2SO_3:





This reaction was applied on fiber II (Bemberg rayon having grafting content of 101 wt.-%), and polysulfonic acid was obtained. For this addition reaction, Na_2SO_3–H_2O and Na_2SO_3–$NaHSO_3$–H_2O were most effective. In $NaHSO_3$–H_2O, the reaction ratio was very small. The results obtained at 45°C., in 20 hr. are listed in Table VII. The reaction ratio was calculated by the titration of the generated HCl from the sulfonic acid and 1*N* NaCl solution. For comparison, S analysis was carried out by the Carius method.

Effect of the concentration was examined for the GMA-grafted cellulose in Na_2SO_3–$NaHSO_3$–H_2O system, the most proper concentration being 20% (Fig. 17). The effect of the reaction temperature for the 20% Na_2SO_3–

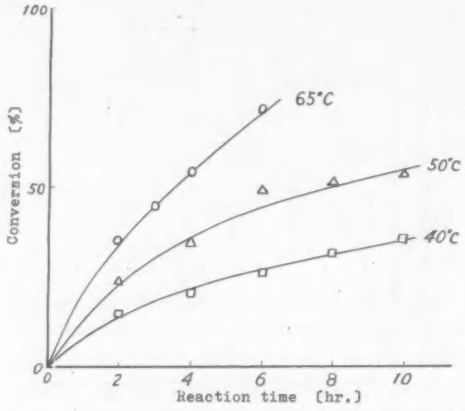


Fig. 15. Effect of temperature on the formation of quaternary ammonium salt in benzyl chloride-DMF (50:50) solution.

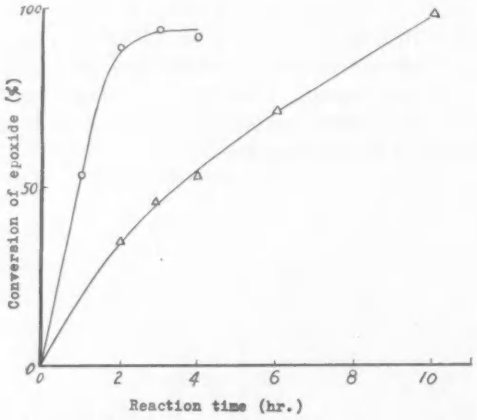


Fig. 16. Effect of solvent on the formation of the quaternary ammonium salt at 65°C. in benzyl chloride (50 wt.-%) solutions: (○) in water; (△) in DMF.

TABLE VI

Effect of the Solvent on the Formation of the Quaternary Ammonium Salt in 50% Benzyl Chloride Solution, Temp. 65°C., Time 6 hr.

Solvent	Dielectric constant D at 25°C.	Conversion of epoxide, %
Acetone	20.7	55.2
DMF	26.6	86.7
Nitrobenzene	34.9	58.9
Benzene	2.28[a]	55.2
Bulk[b]	—	47.8

[a] At 20°C.

[b] Without solvent, for 5 hr.

TABLE VII
Introduction of —SO_3Na Group, Temp. 45°C., Time 20 hr.

Reaction medium	pH		S, wt.-% (Carius method)	Conversion of epoxide, %
	Before reaction	After reaction		
Na_2SO_3 H_2O (Na_2SO_3 20 wt.-%)	9.5	11.9	6.00	62.3
Na_2SO_3–$NaHSO_3$–H_2O (Na_2SO_3 10 wt.-%, $NaHSO_3$ 7 wt.-%)	6.8	6.6	6.60	65.7

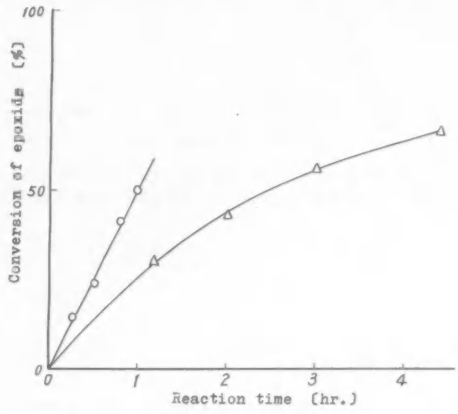


Fig. 17. Effect of concentration on reaction of fiber II in $NaHSO_3$–Na_2SO_3–H_2O systems: (○) 20% solution; (△) 10% solution.

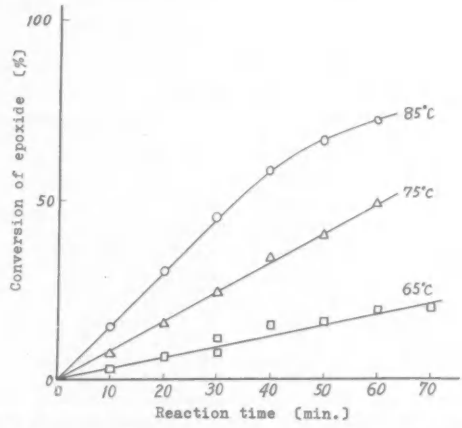


Fig. 18. Dependence of reaction rate on the temperature.

$NaHSO_3$–H_2O system is shown in Figure 18. The Na_2SO_3 and $NaHSO_3$ systems are compared in Figure 19.

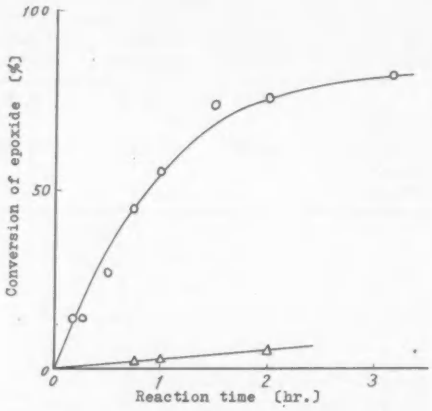
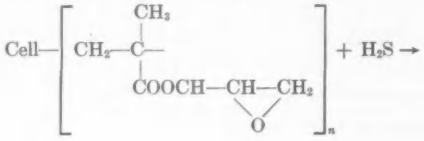


Fig. 19. Comparison of the reactivity of Na_2SO_3 and $NaHSO_3$ with fiber II at 75°C.: (○) 20% aqueous Na_2SO_3: (△) 20% aqueous $NaHSO_3$.

GMA-grafted cellulose fiber can react with H_2S to form polythiol:



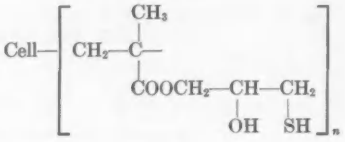


TABLE VIII
Introduction of —SH Group into Fiber II at Room Temperature, Time 10 hr.

Reaction medium	—SH, mole-% (determined by I_2 method)	Ion exchange ability for Ag^+, $\times 10^3$, mole/g.	Infrared spectrum[a]		
			Epoxy group	—CH_2S—	—CH_2SH
H_2S–DMF	40	1.28	0	+	+
H_2S–DMF–Pyridine	38	1.21	0	+	+
NaSH–DMF–H_2O	0	0	0	+	0
NaSH–H_2O	0	0	0	+	0

[a] Zero (0) denotes group is absent; plus (+) denoted group is present according to infrared spectrum.

Table VIII shows the results obtained from the reaction of GMA-grafted Bemberg rayon (of grafting content 101 wt.-%, epoxy value 98%) in the systems of H_2S–DMF (6 wt.-% H_2S), H_2S–DMF–pyridine (6:93:1 by wt.), NaSH–DMF–H_2O (3:92:5 by wt.), and NaSH–H_2O (5 wt.-% NaSH) at room temperature in sealed tubes.

Analysis of the introduced —SH by iodometry agrees well with the values calculated from the ion exchange abilities of Ag^+. Epoxy groups are consumed by the treatment of NaSH and the produced —SH groups seem to change into —CH_2—S—S—CH_2— linkages. Accordingly, for the introduction of —SH groups, the reaction in H_2S–DMF system is best suited. In this case no catalytic reaction of pyridine was observed. Figure 20 shows the reaction ratio–time curves for H_2S–DMF system. Analyses

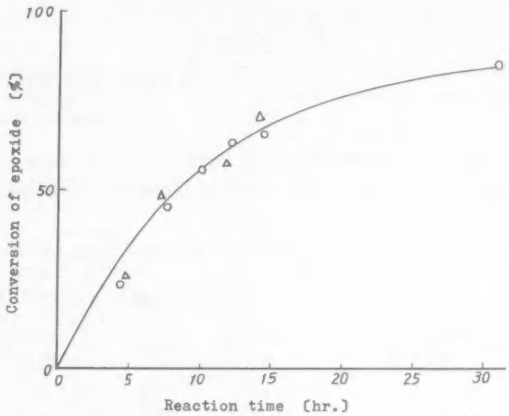


Fig. 20. Relation between conversion and reaction time as measured by different methods: (O) I_2; (△) $AgNO_3$.

of SH group by iodometry and Ag^+ ion exchange ability are in good agreement. This indicates that the polythiol fiber might be able to be used as a heavy metal ion-exchange fiber.

The change of the SH groups in this polythiol fiber was followed by iodometry, and the obtained result was several per cent loss in 140 hr.

TABLE IX
Oxidation of —SH Group in Fiber II Treated by H_2S on Standing in the Air at Room Temperature

Time of standing, hr.	Extent of decrease of —SH group, %
17	3
70	5
140	7.5

Two reaction products can be expected from the reaction of GMA-grafted Bemberg rayon and thioglycolic acid:

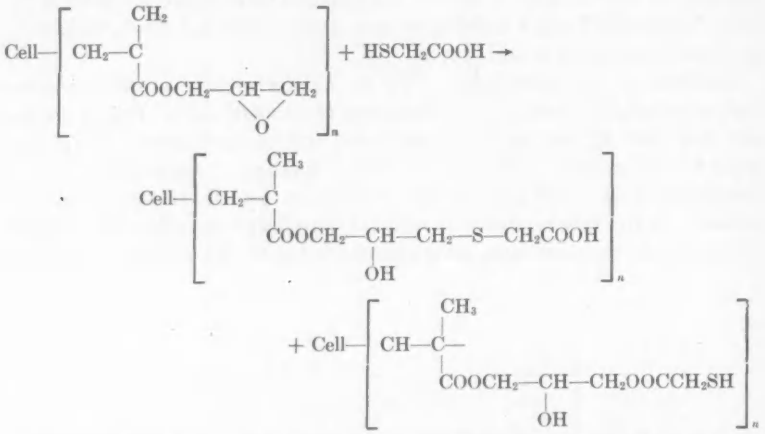


Table X shows the results obtained from the reaction of GMA-grafted Bemberg rayon (GMA 4.06 + 10^{-3} mole/g. fiber) and thioglycolic acid.

TABLE X
Reaction of Fiber II with Thioglycolic Acid in Various Conditions[a]

Reaction medium	Additive (equimolar to thioglycolic acid)	—SH produced		—COOH produced	
		mole/g. $\times 10^4$	%	mole/g. $\times 10^4$	%
H_2O	None	10.3	25.4	7.5	18.5
H_2O	Pyridine	7.7	19.0	1.8	4.4
H_2O	$NaHCO_3$	5.8	14.3	1.4	3.4
H_2O	Pyridine, $NaHCO_3$	3.9	9.6	0	0
DMF	None	5.6	13.8	1.3	3.2
DMF	Pyridine	7.4	18.2	4.7	11.5

[a] Fiber II content of grafting 4.06 $\times$ 10^{-3} mole/g. fiber; thioglycolic acid concentration 15 wt.-%; temperature 55°C., time 15 hr.

Amphoterization of acrylonitrile (AN)–GMA copolymer by the treatment of amino acids was reported in the previous paper.[1] Amphoterization of fiber II can be similarly performed by the reaction of amino acids. Figure 21 shows the reaction of fiber II with amino acid. Towards the end of the reaction, the amount of the reacted epoxy group becomes twice the amount of the reacted amino acids.

This fact shows that primary amine of the amino acid reacts as a bifunctional group. But it reacts as a monofunctional group at the beginning of the reaction, because at that time the amount of the reacted epoxy group agrees with that of amino acid.

The dyeability of fiber II treated by amino acids is shown in Table XI.

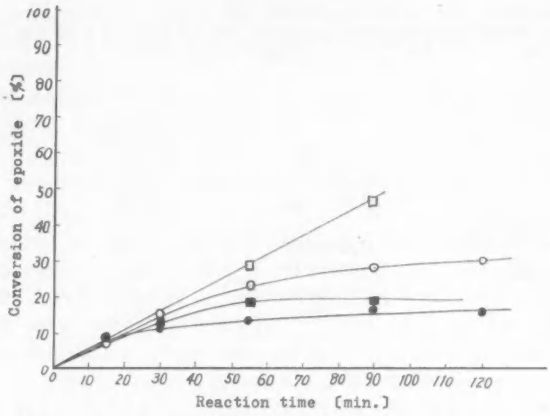


Fig. 21. Reaction of fiber II with alanine at 65°C.: (○) calculated from consumed epoxide; (●) calculated from N content; (□) calculated from consumed epoxide; (■) calculated from N content.

TABLE XI
Dyeability of Fibers Amphoterized with Various Amino Acids

Amino acid	Grafting content of fiber II, %	Reaction solvent	Reaction time, min.	Conversion, %	N, % (Kjeldahl)	Dyeability	
						Acid dye[a]	Basic dye[b]
Alanine	120	H_2O	90	21.0	1.15	+++	+++
Glycine	120	H_2O	90	19.0	1.05	+++	+++
Leucine	120	H_2O	90	16.1	0.89	+++	+++
Taurine	120	H_2O	90	13.5	0.77	+	+++
Lysine	95	H_2O	120	5.5	0.58	+++	+
Homocysteinic acid	95	H_2O	120	0	0	+	+++
Threonine	95	H_2O	120	4.8	0.51	+	+++
(Bemberg)	0	—	—	—	—	0	0

[a] Acid dyes: Acid Brilliant Scarlet 3R, Acid Orange II.
[b] Basic dyes: Malachite Green, Fuchsine, Rhodamine B.

As can be judged from the table, treated fibers show excellent affinity both to acidic and basic dyes, and it can be said that the amphoterization is almost complete.

Absorption ability of amino acid-treated fiber II was examined by the use of glutamic acid. Table XII shows the absorption equilibrium at room temperature. All types of amino acid-treated fiber II absorb glutamic acid, but the lysine-treated fiber shows the best absorption ability.

The effect of solvents, and catalytic action of pyridine are examined in this reaction. Reaction ratio–time diagrams are given in Figure 22. The

TABLE XII
Absorption at Room Temperature of Glutamic Acid on Fiber II (Grafting Content 126 wt.-%) Treated with Amino Acids

Amino acid	Solvent	Amino acid/fiber, mole/g.	Amount absorbed at equilibrium, mole/g.
Lysine	H_2O–DMF	0.516	0.364
Homocysteinic acid	H_2O–DMF	1.133	0.418
Threonine	H_2O–DMF	1.073	0.335
Lysine	H_2O–pyridine	0.649	0.418
Lysine	H_2O–DMF	0.883	0.539

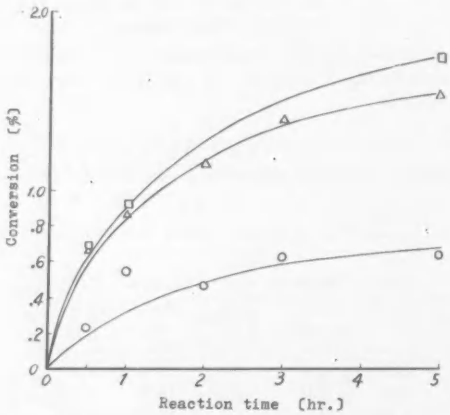


Fig. 22. Reaction of fiber II with lysine in various media at 65°C.: (○) water; (△) water containing 0.45 wt.-% pyridine; (□) 1:1 mixture of DMF and water.

results in Figures 21 and 22 indicate that the reaction velocity is larger in the water–DMF system than in water and that the catalytic action of pyridine does exist. The reactivity of amino acids to fiber II is smaller than that of amine.

EXPERIMENTAL

Materials

GMA. GMA was prepared by the method described in a previous paper,[1] and the physical constants were as follows: b.p.$_{15}$ 85°C.; n_D^{25} 1.4476; purity 100.0% (calculated from analytical result by means of the $Na_2S_2O_3$ method[4]).

Ceric Dioctyl Sodium Sulfosuccinate. Oil-soluble ceric salt was prepared from ceric ammonium nitrate and dioctyl sodium sulfosuccinate.[5]

Dioctyl sodium sulfosuccinate was obtained from the reaction between dioctylmaleate and sodium bisulfite and purified by extracting unreacted components with ether.

Ceric Ammonium Nitrate. This was a commercial guaranteed reagent from G. F. Smith Chemical Company.

Styrene. Commercial Styrene was dried over silica gel and distilled under reduced pressure under N_2 gas atmosphere; $b.p._{31}$ 53.0–53.2°C.

Alcohols. Ethyl, isopropyl, *n*-butyl, *sec*-butyl, and *tert*-butyl alcohol were dried over calcium oxide and distilled (ethyl alcohol, b.p. 78.5°C.; isopropyl alcohol, b.p. 82.4°C.; *n*-butyl alcohol, b.p. 118.0–118.5°C.; *sec*-butyl alcohol, b.p. 99.5–100°C.; *tert*-butyl alcohol, b.p. 82.5°C.).

Benzyl, *n*-octyl, and 1-phenylethyl alcohol and 2,3-butenediol were purified by distillation under reduced pressure (benzyl alcohol, $b.p._{13}$ 98.5–99.0°C.; 1-phenylethyl alcohol, $b.p._{16}$ 95.5–96.0°C.; *n*-octyl alcohol, $b.p._{24}$ 101.0–102.5°C.; 2,3-butenediol, $b.p._{13}$ 86.0–86.5°C.).

Tetramethylene Diisocyanate. The diisocyanate was prepared from adipic acid hydrazide by the Curtius reaction,[6] $b.p._{20}$ 112–113°C.

Bemberg Rayon and Viscose Rayon. The characteristics of the rayons used are shown in Table XIII.

TABLE XIII

	Dry strength, g./den.	Dry elongation, %	D.P.	Crystallinity, %
Bemberg rayon	2.5–2.6	12–14	470–490	50–55
Viscose rayon	2.84	21.0	500–600	40–45

The rayons were dipped in sodium laurylsulfonate and the detergent washed out thoroughly with hot water.

Cellophane. Commercial cellophane was used after removal of softener. Before the grafting, cellophane was dipped in warm water (50–60°C.), the water being exchanged several times to remove ethylene glycol added as a softener.

Polymerization of Styrene

In a round flask fitted with a reflux condenser and N_2 gas inlet tube, were placed styrene (0.1 mole), alcohol (0.01 mole), and oil-soluble ceric salt (1.5 wt.-% of monomer). Polymerization was carried out at 70°C. for 9 hr. with nitrogen being bubbled through. The polymer obtained was precipitated in methanol and dried in a vacuum desiccator.

Reaction of Polystyrene with Tetramethylene Diisocyanate

In a three-necked flask equipped with a stirrer, a dropping funnel, and a reflux condenser were placed polystyrene ($\bar{M}_v = 6.4 + 10^4$) prepared by the procedure described above, toluene, and traces of dibutyl tin dilaurate

and triethylenediamine as catalysts. The flask was heated on a water bath at 50°C., and a toluene solution of tetramethylene diisocyanate was added dropwise over the course of 40 hr.

The intrinsic viscosities of the polymer which was treated as described above, and of the original polystyrene were determined in toluene at 30°C. The viscosity-average molecular weight $\bar{M}_v$ was computed from the equation:

$$[\eta] = 1.2 \times 10^{-4} \bar{M}_v^{-0.07}$$

Graft Copolymerization

The fiber was dipped in a 50–100-fold amount of water, heated for 5–10 min. to remove air absorbed on the fiber, cooled to room temperature under N_2 gas atmosphere, and the GMA was added. After all the GMA had dissolved in water, the graft polymerization was initiated by addition of ceric salt.

Determination of Epoxy Value

The epoxy value of grafted fiber was determined by the HCl–DMF method.[1] When basic materials such as pyridine and amines were present, aqueous $AgNO_3$ was used for the titration of excess HCl.

Reaction of Fiber II with Dyes

The composition of the dye bath was as follows: fiber II, 1 part; dye, 0.02 part; Na_2SO_4, 0.05 part; pyridine, 0.02 part; water, 100.00 parts; reaction temperature, 60–80°C.; reaction time, 30–60 min.

The degree of exhaustion was measured by electric photometer.

Fastness to light was determined with a Fedeo tester after irradiation for 30 hr.

To determine the fastness to washing; the fiber was treated in a Laundrometer with 0.2 wt.-% aqueous Na_2CO_3 at 70°C. for 45 min.

Determination of Quaternary Ammonium Chloride by Ion Exchange

The ion exchange fiber which was obtained by treating fiber II with amine and benzyl chloride was dipped in water and 1*N* aqueous KNO_3 was added. The desorbed Cl^- was titrated with 0.1*N* aqueous $AgNO_3$. From the amount of $AgNO_3$ consumed, the ion exchange ability was calculated.

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Synopsis

Reactive cellulose fiber (fiber II) was prepared by grafting glycidyl methacrylate (GMA) which has an epoxy ring as a reactive group to cellulose fiber (Bemberg rayon and viscose rayon) by redox reaction of ceric salts with cellulose. From the x-ray diffraction photograph, it was observed that the crystallinity and the orientation of the fiber II were not changed after the grafting. The cross section of the chemically dyed fiber II showed that the dyeing had taken place chiefly at the outer layer of the fiber when the graft content was not large. Consequently, the grafting of GMA to cellulose fiber is considered to have proceeded from the outer layer of the fiber. Fastness to washing of the fiber dyed by the chemical bonding increased as expected, but the fastness to light decreased to some extent. Fiber II was aminated by introducing basic amino groups by the chemical reaction of the fiber with primary, secondary, or oxyamines. Reactions with amino or aminosulfonic acids imparted to the fiber II some amphoteric properties. By the formation of quaternary ammonium hydroxide from aminated fiber II, an anion exchange fiber was obtained. A cation exchange fiber was prepared by introducing sulfonic acid group to fiber II with sodium sulfite. Furthermore, it was found that the fiber containing a mercapto group was easily prepared by the addition reaction of hydrogen sulfide with fiber II under pressure. The fiber thus treated showed silver ion exchange property.

Résumé

On a préparé une fibre cellulosique réactive (II) par greffage du methacrylate de glycidyle(I), comportant un cycle époxy réactif, sur une fibre de rayonne (Bemberg ou Viscose). Ce greffage est catalysé par les sels cériques (réaction redox). Les clichés aux rayons X de la fibre (II) montrent que ni la cristallinité, ni l'orientation ne sont détruites par le greffage. La fibre (II) peut être teinte de façon permanente grâce à la combinaison chimique du colorant. Cette combinaison se forme par réaction additionnelle des groupements aminés ou phénoliques du colorant avec les groupes époxy du copolymère greffé (à 60–80 = pendant 30–60 min. avec la pyridine comme catalyseur). D'après l'aspect de la section transversale de la fibre (II) chimiquement teinte, on voit que la teinture s'effectue principalement sur la couche extérieure de la fibre lorsque le degré de greffage n'est pas très grand. En conséquence on admet que le greffage procède à partir de la couche extérieure de la fibre. La solidité au lavage de la fibre (II) teinte chimiquement s'accroit, comme prévu, tendis que la solidité à la lumière diminue quelque peu. La fibre peut être animalisée par l'introduction de groupes aminés basiques, introduction due à la réaction chimique de la fibre avec les amines primaries ou sécondaires ou oxyamines. La fibre (II) acquièrt des propriétés amphotères par réaction avec des acides aminés ou aminosulfonés. On a obtenu une fibre échangeuse d'anions par formation des groupes d'hydroxyde d'ammonium quaternaire sur la fibre (II) aminés. On a préparé également une fibre échangeuse de cations par introduction du groupe sulfoné sur la fibre (II) au moyen du sulfite de sodium. L'hydrogène sulfuré sous pression s'additionne facilement à la fibre (II), en formant des groupes mercapto. Cette fibre est alors échangeuse d'ion argent.

Zusammenfassung

Durch Aufpfropfen von Glycidylmethacrylat (I) mit einem Epoxyring als reaktive Gruppe auf Zellulosefaser (Bemberg-Rayon oder Viscose-Rayon) mittels Redoxreaktion eines Ceri-salzes mit der Zellulose wird eine reaktionsfähige Zellulose (II)-Faser darge-

stellt. Aus den Röntgenaufnahmen der Faser (II) ergibt sich, dass bei der Pfropfung der Kristallaufbau und die Orientierung der Faser nicht verändert werden. Die Faser (II) zeigt permanente Färbung infolge chemischer Bindung des Farbstoffes (Bindung durch die ringöffnende Additionsreaktion des Epoxyringes des Pfropfpolymerisats mit den Amino- oder phenolischen Hydroxylgruppen der Farbstoffmoleküle, bei 60–80° und während 30–60 Minuten mit Pyridin als Katalysator). Der Querschnitt der Faser (II) mit chemisch gebundenem Farbstoff zeigt, dass bei nicht zu hohem Pfropfungsgrad, die Färbung hauptsächlich in der äusseren Schichte der Faser stattfindet. Man kann folglich sagen, dass die Pfropfung des Glycidylmethacrylats auf Zellulosefaser von der äusseren Schicht der Faser aus fortschreitet. Die Waschbeständigkeit der Faser (II) steigt, wie vorauszusehen, an, während die Lichtbeständigkeit etwas abnimmt. Die Faser (II) kann durch Einführung von basischen Aminogruppen, und zwar durch Reaktion dieser Faser mit primären und sekundären Aminen oder Oxyaminen animalisiert werden. Reaktion mit Amino- oder Aminosulfosäuren verleiht der Faser (II) amphotere Eigenschaften. Aus der aminierten Faser (II) kann man durch Quaternisierung der Aminogruppen Anionenaustauscherfasern herstellen. Andererseits können durch Einführung von sulfonsauren Gruppen in die Faser (II) mit Natriumsulfit Kationenaustauscherfasern dargestellt werden. Schwefelwasserstoff unter Druck führt zu einer Additionsreaktion an die Faser (II). Die so erhaltene Mercaptofaser besitzt Silberionenaustauschereigenschaften.

Discussion

G. N. Richards (*A.M.F., Reading, Great Britain*): (*1*) Is there any evidence of the formation of alkali-labile linkages in the cellulose molecule by action of ceric ion during the grafting reaction?

(*2*) Is any information available on the mechanical properties of grafts prepared from rayons of differing crystallite size?

Y. Iwakura: (*1*) There is no positive evidence of the formation of alkali-labile linkages and I guess that during the grafting reaction using ceric ion as catalyst, the degradation of cellulose molecule has not so much occurred.

(*2*) We have no positive information about your question but I think that from the results of the mechanical properties of the grafted viscose and Bemberg rayon, the grafting has been carried out only at the non-crystalline parts (the amorphous parts) in the cellulose molecule without the effect of crystallite size.

JOURNAL OF POLYMER SCIENCE: PART C NO. 4, PP. 699–705

Internal Pressure of Block Copolymers

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INTRODUCTION

A research program has been begun in these laboratories the aim of which is to determine the correlations between internal pressure P_i and composition and structure of natural and synthetic polymers and to show what kind of information can be derived from a study of this quantity.[1]

The internal pressure P_i, defined by the identity:

$$P_i = (\partial U/\partial V)_T \tag{1}$$

(where U is internal energy, V is volume, and T is temperature) has been extensively studied, especially in relation to the cohesive energy density (C.E.D.) of low molecular weight liquids, by Hildebrand et al.;[2] recently, Gee et al.[3,5] have applied this kind of measurement to high polymers, showing how useful it is in giving information about structure and properties of macromolecules.

As a part of a wider program of measurements on polymers, both in solution and in solid state, we have started research on the internal pressure of block copolymers.

The aim of this work is a general one: try to correlate the properties of a copolymer with those of the two (or more) homopolymers.

The samples used in this work are block copolymers of polydimethylsiloxane (PDS) and polyethylene oxide (POE) or polypropylene oxide (POP), which can be represented by the formula:

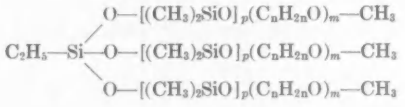

Table I shows all the data about the composition of the samples used; these were obtained from Union Carbide Co. through Chem-Plast (S.R.L.), Milan.

The polyether portion of sample L520 is a random copolymer of equal parts of POP and POE.

TABLE I
Composition Data of Studied Samples[a]

Sample	M.W. siloxane portion, mole fraction	M.W. POE chain, mole fraction	M.W. (POE + POP) chain, mole fraction	M.W. POP chain, mole fraction
L520	1500/0.25	—	1530/0.75	—
L521	800/0.25	750/0.75	—	—
L522	800/0.25	—	—	714/0.75

[a] The first number is the molecular weight of the portion indicated on the column head; the second number is its mole fraction in the copolymer.

EXPERIMENTAL

A full description of the experimental technique has been given previously;[6] thus we will give here only a brief summary.

The first and second thermodynamic principles allow us to write eq. (1) as follows:

$$P_i = (\partial U/\partial V)_T = T(\partial P/\partial T)_V - P \tag{2}$$

so what we need to know P_i is the quantity $(\partial P/\partial T)_V$.

The sample, in our case liquid, at room temperature (except sample L521, for which the measurements have been done immediately above the melting point, m.p. 35°C.) is degassed and put in a Pyrex glass cell, shown in Figure 1.

The cell is immersed in a pressure vessel filled with transformer oil and accurately thermostated; the level of mercury inside the capillary C is

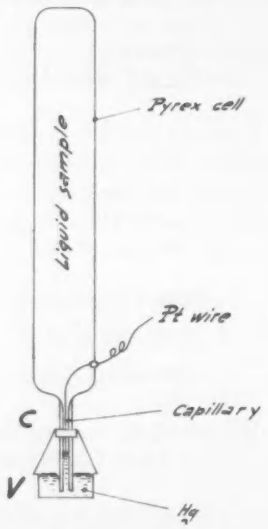

Fig. 1. Pyrex cell for internal pressure measurements on liquid samples.

detected by an electric lamp connected with the platinum wire and the mercury in V.

The determination of $(\partial P/\partial T)_V$ is actually done by measuring, at different temperatures over a range of about half a degree, the pressure required to keep constant the volume of the sample, i.e., to keep the mercury always in contact with the platinum wire (lamp on).

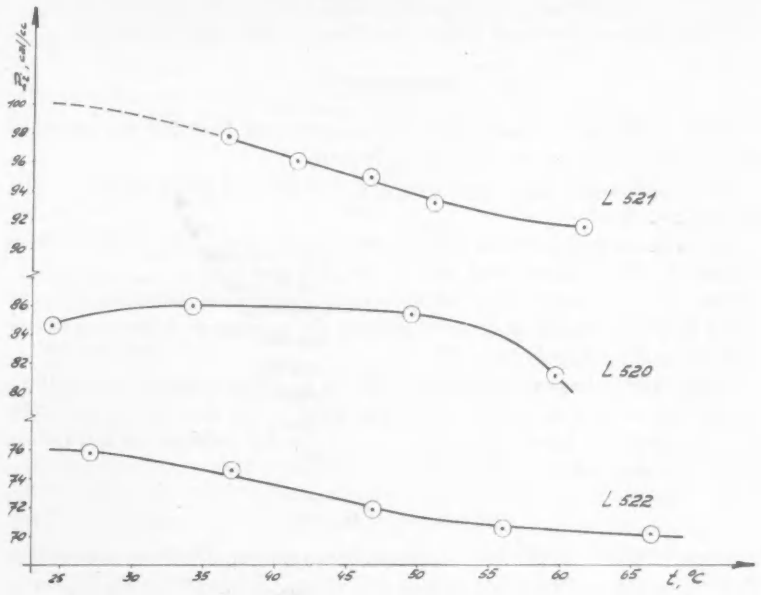

Fig. 2. Internal pressure vs. temperature for block copolymers.

Values of $(\partial P/PT)_V$ so measured, called in the following γ_{sp} must be corrected for the thermal expansion coefficient and compressibility of the Pyrex cell.

It is easy to see that γ, the corrected value of γ_{sp}, is given by:

$$\gamma = \gamma_{sp}[1 + (\alpha_g/\alpha_p) - (\beta_g/\beta_p)] \tag{3}$$

where α_g and α_p are thermal expansion coefficients of the Pyrex and polymer, respectively, and β_g and β_p compressibility of the glass and the polymer, respectively.

As the polymer compressibility β_p is not known, we can use instead the ratio α_p/γ_{sp} (remembering the relationship $\gamma = \alpha/\beta$); it is easy to show numerically that this approximation is well within the experimental error.

Table II collects numerical values used to correct γ_{sp}.

The measurements of P_i have been done for the three samples over a range of temperatures. Figure 2 shows the values obtained and their behavior with temperature.

TABLE II
Thermal Expansion Coefficients and Compressibilities used to Correct γ_{sp}[a]

Material	$\alpha \times 10^4$, °C.$^{-1}$	$\beta \times 10^6$, atm.$^{-1}$
L520	7.8	—
L521	7.5	—
L522	7.5	—
Pyrex	0.099	3

[a] Values for copolymers were derived from Union Carbide publications.

DISCUSSION

In the following we will make the assumption that for any mixture the volume change on mixing (ΔV_M) is zero.

Let us call A and B, respectively, the siloxane and ether portion of the studied copolymers.

It is reasonable to assume that, in the liquid state, there will be three different kinds of interactions, namely AA, BB, and AB.

The first two kinds are the same as in the pure homopolymers, whereas mixed interactions AB are characteristic of the mixture A + B, or, as in our case, of the block copolymers AB.

Hildebrand[7a,b] has extensively studied the problem of mixed interactions in the case of simple liquids (assuming $\Delta V_M = 0$), showing that, in the great majority of cases, the energy ϵ_{AB} of the AB interaction can be expressed in terms of ϵ_{AA} and ϵ_{BB} by the equation:

$$|\epsilon_{AB}| = \sqrt{\epsilon_{AA} \cdot \epsilon_{BB}} \tag{4}$$

and this, at least qualitatively, corresponds to the experimental observation that the change of enthalpy during the mixing of simple liquids is greater than zero ($\Delta H_M > 0$).

From eq. (4) or, less restrictively, from the assumption that $\Delta H_M > 0$ it follows that the internal pressure $P_{i,M}$ of a mixture must be less than the average value $\overline{P_{i,M}}$:

$$\overline{P_{i,M}} = \phi_A P_{i,A}(\beta_A/\beta_M) + \phi_B P_{i,B}(\beta_B/\beta_M) \tag{5}$$

where ϕ_A, ϕ_B are volume fractions, $P_{i,A}$, $P_{i,B}$ are internal pressures of the pure components, β_A, β_B, and β_M are the compressibilities of, respectively, components A, B, and mixture; β_M is given by $\phi_A\beta_B + \phi_B\beta_B$.

Equation (5) is therefore valid for a mechanical mixture of two immiscible substances A and B.

Equation (5) can be expressed in the simpler form:

$$\bar{\gamma}_M = (\partial P/\partial T)_v = (\phi_A\alpha_A + \phi_B\alpha_B)/(\phi_A\beta_A + \phi_B\beta_B) \tag{6}$$

From eq. (2) it can be seen that $T\gamma$ is much greater than P ($T\gamma$ between 3–4000 atm., P = 1 atm.) therefore γ is directly proportional to P_i; this means that what we said about eq. (5) is valid also for eq. (6), and experimental values of γ_M will be less than the values $\bar{\gamma}_M$ calculated from eq. (6).

This conclusion applied when the interactions present in a mixture are due to van der Waals forces.

However, when a mixture presents strong associations or particularly organized structures, it is possible to have negative heats of mixing ($\Delta H_M < 0$) and therefore experimental values of γ_M (or $P_{i,M}$) greater than those calculated from eq. (6) (or eq. (5)).

Table III refers to mixtures of simple liquids on which Westwater et al.[8] have measured γ_M.

TABLE III
Mixtures of Simple Liquids

Mixture	ϕ_A, volume fraction of first component	$\bar{\gamma}_M$, atm./°C.[a]	γ_M, atm./°C.[b]
Heptane-acetone	0.666	9.48	9.00
Heptane-carbon tetrachloride	0.603	9.66	9.38
Heptane-benzene	0.622	9.85	9.59
Benzene-carbon tetrachloride	0.479	12.20	11.73
Benzene-carbon disulfide	0.596	12.75	12.00
Carbon disulfide-acetone	0.451	11.86	11.42

[a] Values of $\bar{\gamma}_M$ calculated from eq. (6). [b] Values of γ_M measured by Westwater et al.[8]

In column 3 are shown values of $\bar{\gamma}_M$ calculated through eq. (6); as it can be seen, values of γ_M are effectively lower than the calculated ones.

We are measuring in our department internal pressures of polymer solutions; Table IV refers to a solution of polydimethylsiloxane (M.W. 1.6×10^4) in benzene. This mixture, characterized by a $\Delta H_M > 0$, confirms again the prevision with a great difference between γ_M and $\bar{\gamma}_M$.

Having shown what the situation is for "normal" mixtures, let us turn now to our block copolymers.

TABLE IV
Comparison between Calculated and Observed Values of γ_M for a Mixture PDS-Benzene

Mixture	ϕ_P, volume fraction of polymer	$\bar{\gamma}_M$, atm./°C.	γ_M, atm./°C.
PDS-benzene	0.584	0.9	8.5

TABLE V
Comparison between Calculated and Observed Values of γ_M for Copolymers at 25°C.

Block copolymer	$\bar{\gamma}_M$, atm./°C.	γ_M, atm./°C.
L 520	11.1	11.8
L 521	12.1	13.9
L 522	9.1	10.7

Table V gives the comparison between calculated and experimentally observed values of γ, at 25°C.

It is very interesting to note that, in contrast with what we have seen before, values of γ_M are all consistently higher than the calculated ones.

For what we said before, this is an indication that our liquids present an associated structure, very likely due to the large difference between P_i and cohesive energy densities[2] of constituent homopolymers, which can explain also their immiscibility.

The larger values of γ_M in comparison with $\bar{\gamma}_M$ are connected with the organized structure characteristic of this type of block copolymers—structure which probably is different from that existing in the pure homopolymers.

Similar cases of organized structures have been revealed[9] by small-angle x-ray diffraction on concentrated solutions of polystyrene–POE block copolymers.

Due to the interest of these studies, we are extending our P_i measurements to polystyrene–POE block polymers having a wider range of composition and molecular weights.

Note: Samples of our copolymers have been sent, through the kind interest of Prof. H. Benoit, to the Centre de Recherches sur Les Macromolecules of Strasbourg, and analyzed by small-angle x-ray diffraction by Mr. Skoulios, who has found the presence of an organized lamellar structure.

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Synopsis

Internal pressure measurements have been applied to the study of polydimethylsiloxane–polyether block copolymers. Due to the incompatibility of the homopolymers, these copolymers present a highly organized structure, in which interactions between chemically different chains are avoided as much as possible.

Résumé

L'on a étudé des copolymères séquencés de polydiméthylsiloxane–polyéther au moyen de la mesure des pressions internes. L'incompatibilité des homopolymères a pour conséquence la formation d'une structure organisée chez les copolymères séquencés correspondants, dans laquelle les séquences sont arrangés de manière à éviter le plus possible les interactions entre les parties chimiquement différentes.

Zusammenfassung

Messungen des inneren Druckes an verschiedenen Blockpolymeren von Polydimethylsiloxan–Polyether wurden auageführt. Als Folge der gegenseitigen Unverträglichkeit der Homopolymeren, haben die entspreche den Pfropfcopolymere eine hoch organisierte Struktur, die durch Vermeidung der Wechselwirkung zwischen der chemisch verschiedenen Ketten verursacht wird.

JOURNAL OF POLYMER SCIENCE: PART C NO. 4, PP. 707–730

Elastomeric Polycarbonate Block Copolymers*

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INTRODUCTION

Linear aromatic polycarbonates derived from bisphenols such as 2,2-bis(4-hydroxyphenyl) propane (bisphenol-A) represent an increasingly important new class of condensation polymers. Early papers by Schnell,[1] Fox,[2] and Goldberg[3] demonstrated that polycarbonates were readily preparable by three different polyesterification procedures (Fig. 1) and were characterized by unusual property–structure relationships. Poly(bisphenol-A

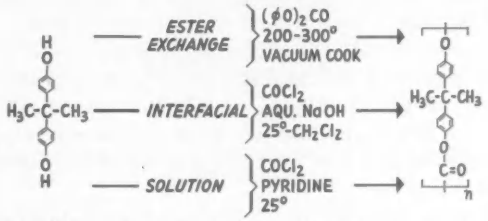

Fig. 1. Major synthetic routes to poly(bisphenol-A carbonate).

carbonate) has been of greatest interest because of the availability of bisphenol-A and because this polymer is a strong, tough, high melting resin possessing a unique combination of desirable properties including: high glass transition (ca. 140°C.), exceptional impact strength (12–16 ft.-lb./in. notch), dimensional stability, creep resistance, thermal-oxidative stability, and a degree of transparency usually found in relatively brittle amorphous polymers. By virtue of this striking property balance and preparative versatility, poly(bisphenol-A carbonate) was considered an intriguing model homopolymer for structural modification. The block copolymer studies reported here were therefore initiated, more than seven years ago, as part of a comprehensive carbonate copolymer study, to generally extend the understanding of polycarbonate property–structure relationships and more particularly to prepare new elastomeric thermoplastic resins.

The introduction of clearly characterized block structural units into linear

* A portion of this work was also presented at the 11th Canadian High Polymer Forum, Assumpsion College, Windsor, Canada, September, 1962.

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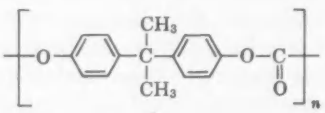
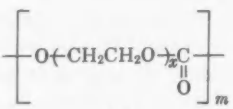
polyesters was difficult until the advent of recently developed low temperature solution and interfacial procenures because conventional high temperature polyesterifications are frequently accompanied by undesirable ester exchange equilibration and thermal degradation. In spite of these problems, copolyesters of reasonably well defined block structures were first prepared and seriously studied by Flory,[4–7] Snyder,[8,9] Coleman,[10] and others[11–13] during the period 1946–1950. Flory's work is particularly significant in defining the comonomer mole ratio dependence of copolymer melting points in crystallizable condensation systems of normal molecular weight distribution. Modification of poly(ethylene terephthalate) by Coleman, through copolymerization with poly(oxyethylene) glycol, further demonstrated that a large weight fraction (but low mole fraction) of a polymeric comonomer could be accommodated with only a slight reduction in the melting point. However, the glass transition temperature in this system displayed a considerable weight fraction sensitivity.

On the basis of the observations of Flory and Coleman, it was considered likely that incorporation of flexible, polar, block segments into the rigid, linear, aromatic carbonate polymer chain would produce unusual thermoplastic elastomers. That this is indeed the case is clearly indicated by the research reported here. This present study involved the use of polyether glycols as comonomers with bisphenol-A. The polymeric glycols considered included poly(oxyethylene), poly(oxyethylene-oxypropylene), poly(oxypropylene), poly(oxybutylene) and poly(oxystyrene). Solution copolycondensation in pyridine was employed exclusively because this technique is uniquely satisfactory for the synthesis of high molecular weight copolymers of this type.

Poly(oxyethylene) systems were investigated in greatest detail for the influence of polymeric glycol molecular weight (1000–20,000) and copolymer composition (5–70 wt.-% glycol) upon properties. The linear polyester chain for these resins contains structural units of bisphenol-A carbonate (I) and poly(oxyethylene) glycol carbonate (II).

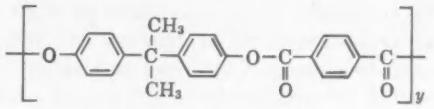


I

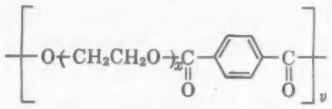


II

An additional structural modification, partial replacement of carbonate linkages by carboxylate (isophthalate, terephthalate, and adipate), was also studied. Resins of this type displayed remarkably different physical and chemical properties as compared with the parent polyether copolymers. In addition to structures I and II, these polymers contain bisphenol-A terephthalate (III) (or isophthalate, adipate, etc.) and poly(oxyethylene) glycol terephthalate (IV) linkages.



III



IV

The very recent renewed interest in polyester block copolymers is important to mention. This approach to new rubbery and semirigid thermoplastics is the subject of a number of patents[13–15] and a particularly pertinent paper by Merrill[16] dealing with polycarbonates. Although Merrill discussed the properties of several types of block copolymers, including those containing poly(oxyethylene) segments, the range of block size and composition covered for this system was apparently limited to the extent that no mention was made of the remarkably snappy and strong elastomers that are a primary subject of the work reported here.

EXPERIMENTAL

A. Materials

Bisphenol-A was recrystallized material of high purity.

Pyridine was reagent-grade, dried and further purified by distillation from barium oxide.

Poly(oxyethylene) glycols were Carbowaxes (Union Carbide) of 1000, 4000, 6000 and 20,000 molecular weight. These polyethers have been shown to have very narrow molecular weight distributions.[17]

Poly(oxyethylene-oxypropylene) glycols were ethylene oxide–propylene oxide block copolymers known as Pluronics (Wyandotte) made by blocking poly(oxyethylene) chains onto both ends of poly(oxypropylene) backbones. Tetrafunctional hydroxyl terminated materials known as Tetronics (Wyandotte) were also copolymerized. The Tetronics are prepared by blocking poly(oxyethylene–oxypropylene) chains onto ethylene diamine.

Poly(oxypropylene) glycol was Dow P2000, poly(oxybutylene) glycol was Dow B1000, and poly(oxystyrene) glycol was Dow S750.

Isophthalic, terephthalic, and adipic acids were repurified reagent-grade materials.

B. Copolymerization Procedure

The block copolymers were prepared according to the following general procedure. A 100-cc. semimicro resin pot reactor was charged with 12.0 g. of the bisphenol–glycol mix dissolved in 75 cc. of pyridine. With rapid and efficient stirring, phosgene was bubbled into the solution at a rate of ca.

0.2 g./min. The temperature was maintained at about 30°C. Phosgene was added until completion of polymerization (10–30% molar excess) as evidenced by rapid thickening of the reaction mixture. The copolymers were usually isolated by precipitation and repeated washing in a Waring Blendor with isopropanol until completely free (by phosphomolybdic acid test) of pyridine and pyridine hydrochloride. Copolymers in the form of finely divided fibrous powders were dried at 80°C. until free of solvent (usually ca. 18–24 hrs.).

Carboxylate tetrapolymers were prepared similarly, the dicarboxylic acid merely being an additional component of the initial solution to be phosgenated.[18,19]

C. Characterization

1. Infrared Analysis

Copolymer compositions were verified using infrared bands characteristic of the $-OCH_2CH_2-$ structure at 3.54 μ (—CH), 7.44 μ ($-CH_2-$), 9.1 μ (—O—) and 10.6 μ (—C—O—). Carbonate-carboxylate polymers were characterized by the absorbance ratio for the carbonyl twin at ca. 5.6 μ (carbonate) and ca. 5.7 μ (isophthalate, terephthalate, or adipate). In all cases, compositions were in good agreement with monomer ratios charged to the polymerization reaction.

2. Water Extraction

To establish that the polymerization products were not physical mixtures containing unreacted glycol or glycol carbonate homopolymer, water extraction during polymer isolation and purification was employed and found to remove no detectable amount of these water soluble materials. Furthermore, polymer isolated by water precipitation and wash was virtually identical to that obtained from nonaqueous isolations.

3. Polymer Compatibility

Further evidence for true copolymerization rather than formation of a polymer mixture was obtained by compatibility studies. Films cast from 7 wt.-% solutions of bisphenol-A carbonate homopolymer mixtures with 4000 Carbowax (containing 14–43% Carbowax) in chloroform were rough, milky, and very weak, indicating incompatibility. Similar results were obtained with poly(bisphenol-A carbonate) mixtures with a poly(oxyethylene) carbonate polymer prepared by phosgenation of 4000 Carbowax in pyridine. This latter homopolymer was obtained as a waxy material melting sharply at 54–56°C. The intrinsic viscosity in *p*-dioxane was 0.56 and a reduced viscosity of 2.2 ($c = 8.0$) was observed in water solution as compared with 0.14 for 4000 Carbowax.

TABLE I

Poly(oxyethylene) Glycol–Bisphenol-A Copolycarbonate Properties: Effect of Glycol Molecular Weight

Carbowax	Wt.-%	Mole-%	[η]	T_g, °C.	Soft. temp., °C.	Wt. loss (200°C., 24 hr.), %	Tensile properties[a] Y psi	U, psi	E, %	TE, ft.-lb./in.³	Temp., °C.	Orientation, %	Elastic recovery, % IER	IER$_0$
1000 CBX	50	18.5	0.70			21.5	830	2360	565	630	25		94	97
							—	5430	320	700	25	64		
							—	290	60	10	120			
4000 CBX	50	5.4	1.08			41.4	460	7030	460	870	25		96	99
							480	10740	280	1010	25	55		
							285	2020	655	460	120			
6000 CBX	50	3.7	0.89			41.9	980	7080	570	1200	25		90	97
							725	10730	305	1180	25	68		
							470	1600	660	425	120			
20000 CBX	50	1.1	Insoluble gel		170–195	29.0								
20000 CBX	30	0.4	>1.6, some gel	128	185–200		4860	6350	195		25			
20000 CBX / 4000 CBX	25 / 25		Insoluble gel		170–190	34.8								

[a] Y = yield; U = ultimate strength; E = elongation; TE = tensile energy.

TABLE II. Properties of Copolycarbonate From 4000 Molecular Weight Poly(oxyethylene) Glycol and Bisphenol-A: Effect of Composition

4000 Carbowax							Tensile properties[a]						Elastic recovery, %	
Wt.-%	Mole-%	$[\eta]$	T_g, °C.	Soft. temp., °C.	Wt. loss (200°C., 24 hr.), %	Stiffness in flexure, cm.kg./°	Y, psi	U, psi	E, %	TE, ft.-lb./in.^{3}	Temp., °C.	Orientation, %	IER	IER_θ
0		1.00	140	210–230	1.0	1.75								
5	0.3	0.81	122		5.0	2.05	9990[b]	8170	110	755	25			
							7440	6230	115	555	80			
							2600	4980	205	550	120			
10	0.6	0.82	111	200–210		2.25	10120[b]	8070	215	—	25			
							5860	6890	225	—	80			
							2830	5270	305	—	120			
30	2.4	1.11	44	195–205	24.1	0.50	5010	7530	205	745	25		20	—
							7600	16450	60	570	25	103		
35	3.0	0.82			27.9		2010	7410	275	940	25		91	90
							1290	7420	260	860	25	22		
40	3.7	1.01			30.2		1240	7320	350	990	25		91	96
							570	8150	290	895	25	26		
							605	2870	585	575	120			
45	4.5	0.82		190–205	35.9		1060	7220	450	1120	25		92	97
							815	9290	315	1120	25	41		
							490	1930	630	445	120			
50	5.4	1.08			41.4		460	7030	460	870	25		96	99
							480	10740	280	1010	25	55		
							285	2020	655	460	120			
55	6.5	0.82			43.6		600	6860	620	1220	25		95	97
							395	9220	385	1210	25	55		
							405	1060	660	265	120			
60	7.9	1.09			49.8		425	5700	660	840	25		93	97
							385	10260	405	1095	25	53		
							250	890	880	280	120			
65	9.6	1.03		170–190			410[b]	4070	740		25			
							310	1235	650		80			
100		0.56		54–56 (m.p.)										

[a] Y = yield; U = ultimate strength; E = elongation; TE = tensile energy. [b] At 2 in./min.

TABLE III
Properties of Additional Polyether Glycol–Bisphenol-A Copolycarbonates

	Wt.-%	[η]	Wt. loss (200°C., 24 hr.), %	Soft. temp., °C.	Tensile properties[a] Y, psi	U, psi	E, %	TE, ft.-lb./in.³	Temp., °C.	IER, %
Pluronic L-62										
(20% polyoxyethylene, 2000 M.W.)	50	0.57	35.6	115–170	1070	3780	590	995	25	94
					—	370	60	20	120	
Pluronic L-64										
(40% polyoxyethylene, 3000 M.W.)	50	0.59	43.0	130–185	915	3810	620	1040	25	94
					—	370	80	25	120	
Pluronic F-68										
(80% polyoxyethylene, 8000 M.W.)	50	0.80	37.8	100–170	925	6330	545	1180	25	94
					450	1540	635	425	120	
Tetronics		Insoluble								
704, 707, 904, 908	50	gel	38–45							
Poly(oxypropylene) glycol										
(2000 M.W.)	50	0.20		160–190						
Poly(oxybutylene) glycol										
(1000 M.W.)	50	0.26		165–195		1830	110	(rubbery cast film)		
Poly(oxystyrene) glycol										
750 (M.W.)	50	0.17		110–125						

[a] Y = yield; U = ultimate strength; E = elongation; TE = tensile energy.

TABLE IV
Properties of Carbonate–Carboxylate Tetrapolymers from Poly(oxyethylene) Glycol and Bisphenol-A

	Wt.-%	Mole-%	[η]	Wt. loss (200°C., 24 hr.), %	Soft. temp., °C.	Tensile properties[a] Y, psi	U, psi	E, %	TE. ft.-lb./in.³	Temp., °C.
4000 CBX	50		0.63	4.6	65–80	280	6310	470	865	25
Isophthalic acid		50								
4000 CBX	25		1.08	7.1	120–160	8540	8190	135	820	25
Isophthalic acid		50	0.75	6.8	30–50	270	3590	310	360	120
4000 CBX	50									
Isophthalic acid		25								
4000 CBX	50		0.30	26.2	35–55					
Isophthalic acid		75								
20000 CBX		50	Insoluble	13.8	30–50					
Isophthalic acid	50		gel							
4000 CBX	50		0.87	13.1	70–90	560	7140	370	830	25
Terephthalic acid		50					(98% elastic recovery)			
4000 CBX	50		0.87	10.7	55–85	145	90	1760	120	25
Adipic acid		50								

[a] Y = yield; U = ultimate strength; E = elongation; TE = tensile energy.

4. X-Ray Diffraction Crystallinity

The hazy appearance of cast copolymer films coupled with snappy elasticity suggested the presence of an ordered structure. Measurement of interplanar spacings by x-ray diffraction confirmed a moderate degree of molecular order arising from the bisphenol-A carbonate segments of the copolymer chain. No crystallinity attributable to the poly(oxyethylene) segments was observed although the poly(oxyethylene) glycols are themselves highly crystalline polymers. This result is in agreement with the findings of Merrill.[16]

D. Polymer Properties

The principle properties determined for the copolymers are summarized in Tables I–IV. Some additional properties, as well as brief descriptions of sample preparations and test methods, are provided below.

1. Test Samples

The types of samples used for property evaluation were as follows.

a. Bulk Polymer. Fluffy, fibrous bulk resin was directly obtained by drying the material precipitated and washed in the Waring Blendor.

b. Cast Film. Films 6–10 mils thick were cast by controlled evaporation of solvent from 7–8 wt.-% chloroform or methylene chloride solutions in 4 × 6 in. polished tins. Following 16–24 hr. air drying and complete solvent removal at 80°C. (generally 16–24 hr.), test pieces were razor cut to the desired size.

c. Compression-Molded Sheet. Sheets 15–20 mils thick were molded above the softening temperature (ca. 200°C.) in an electrically heated press using a 5 in. picture frame mold. Samples were razor cut to size.

d. Transfer-Molded Bars. Pieces, $^1/_8 \times {}^3/_8 \times {}^5/_8$ in. were formed in a press at 195–205°C. by forcing resin from a plasticizing chamber into a hot 5-cavity mold.

2. Intrinsic Viscosity

The intrinsic viscosity of the bulk polymer was determined in reagent grade *p*-dioxane at 30.3°C.

3. Glass Transition Temperature

The glass transition temperature T_g was measured by a thermomechanical technique similar to penetrometer, heat distortion, or Vicat tests; the $^1/_8 \times {}^3/_8 \times {}^5/_8$ in. transfer-molded sample was heated at a rate of 2–3°C./min., and T_g was taken as that temperature at which rapid deformation of the sample began (10 mil deflection) under a 2.5 kg. flexural load applied by a rounded chisel-point ram.

4. Softening Temperature

The temperature range in which the bulk polymer resin softened and lost form under very slight pressure when heated on a hot block melting point apparatus was measured.

5. Thermal-Oxidative Stability

Weight loss of the bulk polymer was measured for duplicate 0.6 g. samples aged in aluminum cups for 24 hr. at 200°C. in an air circulating oven. In addition, cast films aged in an air circulating oven and tensile tested after 24 hr. afforded the results found in Table V.

TABLE V
Aging of 4000 CBX–Bisphenol-A Copolycarbonate Films

4000 CBX, wt.-%	Aging temp. (24 hr.), °C.	Properties of aged film[a]			Remarks
		Y, psi	U, psi	E, %	
5	150				Brittle
	135		9800	15	
10	150				Some portions brittle
10[b]	150				Some portions brittle
30	150				Yellowed, brittle
	125				No discoloration, brittle
	100	2360	5230	235	No change
30[b]	150	2665	3395	235	Little change
	125	2155	5040	220	No change
65	150				Cheesy, brittle
65[b]	150				Weak, somewhat brittle

[a] Y = tensile yield; U = ultimate tensile strength; E = elongation.
[b] Agerite White (0.5 wt.-%) added.

6. Stiffness in Flexure and Flexural Strength

These properties were measured on a German-made Dynstat tester with $^1/_8 \times ^3/_8 \times ^5/_8$ in. transfer-molded bars at a constant bending rate of 20°/min. and using a C weight; bending angle and moment were recorded every 2° and stiffness in flexure was taken as the initial straight-line portion of the angle-moment plot. The yield point was taken as the flexural strength (Table VI).

TABLE VI
Flexural Properties of 4000 CBX–Bisphenol-A Copolycarbonates

4000 CBX, wt.-%	Stiffness, cm. kg./°	Flexural strength, psi
0	1.75	12,950
5	2.05	15,690
10	2.25	16,000
30	0.50	3,850

7. Tensile Properties

Tensile properties were determined on an Instron tester at 20 in./min. crosshead speed using $^1/_2 \times 1^3/_4$ in. samples of cast film. Five tests were taken for each measurement. Elongation was measured with calipers from extension of gage marks on film at break. Tensile energy was automatically recorded on an Instron integrator attachment. Oriented samples were tested similarly.

8. Orientation

Tensile cast film samples were drawn at 25°C. to 80% of ultimate elongation at 2 in./min. and relaxed at 20 in./min.; this cycle was repeated four times. After 18 hr. relaxation the samples were elongated 100% and relaxed.

9. Elastic Recovery

Immediate elastic recovery (% IER) was measured by 100% extension of tensile cast film samples at 25°C. and 2 in./min. followed by 20 in./min. relaxation and caliper measurement of gage marks after 1 min. relaxation; % IER_0 was similarly measured on previously oriented samples.

10. Tensile Impact Strength

Cast film samples, $^1/_4 \times 1^1/_2$ in., and a modified Bragaw[20] technique were employed. A special stainless steel winged tossvise was fabricated for the film samples. By applying Bragaw correction tables and using six or seven samples per test the values in Table VII were obtained at 25°C.

TABLE VII
Tensile Impact Strength for 4000 CBX–Bisphenol-A Copolycarbonates

4000 CBX, wt.-%	Tensile Impact strength, ft. lb./in.[3]
0	133[a]
10	36
30	1410
65	950

[a] Sample size is an important variable in this test. Note that values in the range 40–0 900 are obtainable with samples of large cross section.

11. Solvent-Chemical Resistance

Copolymers were generally soluble in dioxane, chloroform, and methylene chloride and were swollen by benzene and acetone. Compression-molded pieces, $^1/_2 \times 1$ in. and 20–30 mils thick were subjected to a variety of solvent-chemical environments. Results for copolymers containing 5 wt.-% and 30 wt.-% 4000 Carbowax are summarized in Table VIII.

TABLE VIII
Effect of Various Solvent-Chemical Environments Upon 4000 CBX–Bisphenol-A Copolycarbonates

	4000 CBX, wt.-%	Temp., °C.	Time, days	Total wt. change, %	Remarks
Water	5	25	1	+ 0.4	
			3	+ 0.4	
			7	+ 0.4	
		100	1	+ 0.9	
			3	+ 1.2	
			7	+ 1.9	Opaque, brittle
	30	25	1	+ 5.3	
			2	+ 5.9	
			4	+ 6.5	
			7	+ 7.8	
		100	1	+15.9	
10% NaOH	5	25	7	+ 0.1	
		Reflux	1	−46.9	Etched
	30	25	7		Almost completely dissolved
		Reflux	4 hr.		Oily solution
10% H_2SO_4	5	25	7	+ 0.3	
		Reflux	1	+ 0.5	
	30	25	7	—	Yellowed, brittle
		Reflux	1 hr.	—	Purple, distorted
			4 hr.	—	Black, tarry liquid
ASTM #3 Oil	5	25	7	0.0	
		80	7	0.0	
		135	7	+ 6.6	Opaque, brown, brittle
	30	25	7	+ 0.8	
		80	7	+ 6.3	All samples remained tough and flexible
		135	7	+ 8.1	
10% HNO_3	5	25	7	+ 0.6	
	30	25	7	+13.0	Bright yellow; remained tough and flexible
Isopropanol	5	25	7	+ 0.5	
	30	25	7	+ 7.6	
Acetone	30	25	7	+28.0	Opaque, deformed, flexible

RESULTS AND DISCUSSION

A. Copolymerization

The solution polycondensation employed in this study, phosgenation in pyridine at 25–30°C., was a particularly satisfactory route to the desired high molecular weight copolymers for several reasons. Of greatest im-

portance were (*1*) the ability to directly use the various polymeric glycols and dicarboxylic acids, (*2*) the rapid attainment of high molecular weights, and (*3*) the development of a normal molecular weight distribution. The alternative interfacial method would have been complicated by the required preparation of acid chloride or phenolic hydroxyl-terminated glycols. This approach has been reported.[16] However, a more serious problem inherent in interfacial polycondensation is that of abnormal molecular weight distributions. The diffusion-controlled aspect of such polymerizations is greatly influenced by all reaction variables (time, temperature, solvent, catalyst, concentration, and stirring efficiency) resulting frequently in polynodal polydispersity. Reproducibility of the distribution, too, is attainable only by extreme care with the procedure. Since abnormal distribution can profoundly alter properties and invalidates the usual calculations for average monomer unit repeat sequences in copolymers, the interfacial system was avoided. A final qualification was the relative ease of complete purification of solution-prepared polymers as compared with those made interfacially. High temperature ester exchange was not considered due to possible thermal degradation side reactions and the limitation of molecular weight by high melt viscosity.

The preparation of carbonate–carboxylate tetrapolymers by phosgenation of a diphenol–glycol–dicarboxylic acid mixture in an organic base represents a novel polyesterification.[18,19] The many ramifications of this new synthesis have been investigated and will be discussed in detail in a forthcoming comprehensive paper dealing with carbonate–carboxylate copolymers. Briefly, this reaction involves the *in situ* formation of bischloroformates which then react quite rapidly with the dicarboxylic acid to generate carbon dioxide and the desired carboxylate ester linkage.

B. Poly(oxyethylene) Glycol–Bisphenol-A Copolycarbonates

A major portion of the work reported here concerned the use of a model polymeric glycol, poly(oxyethylene) glycol (Carbowax), which was commercially available (from Union Carbide) in polymer-forming purity in a wide range of molecular weights. This material was readily copolymerized with bisphenol-A to linear high molecular weight thermoplastics and thereby permitted the introduction of well defined, flexible, polar block structures into the bisphenol-A carbonate polymer chain. It was also initially considered that the crystalline structure of these polyether glycols might be retained in the copolymers to produce a strong elastomeric pseudo-crosslinked material. This, however, is apparently not the case. Rather, the remarkable snappy elasticity and strength of the Carbowax copolymers must be attributed to the ordering of bisphenol carbonate chain segments facilitated by the increased molecular mobility conferred by the polyether blocks. This observation is confirmed by x-ray diffraction analyses showing no interplanar spacings characteristic of the normally crystalline Carbowaxes.

An equally interesting and related observation concerns the change in stiffness of 4000 Carbowax–bisphenol-A copolycarbonates as a function of composition (Fig. 2). It can be seen that as the concentration of polyether blocks increases in the range 0–1.0 mole-% (0–15 wt.-%) the copolymer flexural modulus increases. Only beyond ca. 20 wt.-% does the expected effect, greater flexibility, occur. It is now considered that this phenomenon is analogous to a similar and surprisingly obscure result with plasticized rigid thermoplastics. Attention is drawn to papers by Gruenwald[21] and Kozlov et al.,[22] wherein Gruenwald in particular discusses

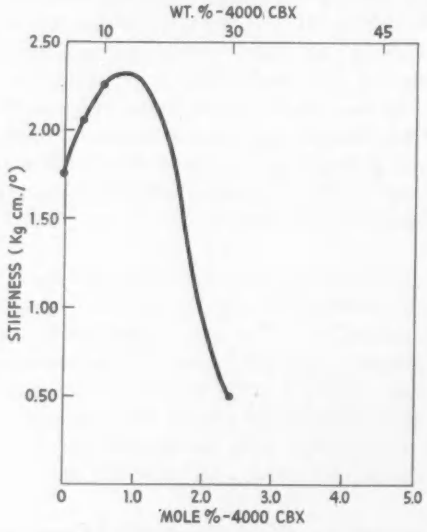


Fig. 2. Stiffness in flexure of 4000 Carbowax–bisphenol-A copolycarbonate as a function of copolymer composition.

lightly plasticized systems and noted that addition of small amounts of plasticizer (0–10%) to poly(vinyl chloride) or poly(bisphenol-A carbonate) results in an initial increase in rigidity as indicated by higher modulus and lower impact strength. It is reasonable to conclude that in the present case at low levels of an internal plasticizer (the polyether blocks) chain mobility is enhanced enough to promote more rapid chain-packing and strong intermolecular association of the very long aromatic carbonate segments, thereby producing a more rigid structure. However, at higher concentrations of the polyether blocks chain motion apparently becomes sufficiently energetic to prevent a high degree of structural order. This effect is magnified by the fact that at higher polyether concentrations the average bisphenol carbonate block length becomes much shorter. A study of x-ray crystallinity as a function of composition would shed further light on this question but was not undertaken as part of the present work.

Before considering the properties of the poly(oxyethylene) glycol copolymer, it is important to indicate the structural changes that accompany molecular weight and compositional variations. The copolymers under consideration contain structural units of types I and II in the linear chain. The value for x is of course predetermined by the choice of the glycol molecular weight. The average repeat sequence of the units, as indicated by n and m, is dependent upon the mole ratio of I and II and is readily

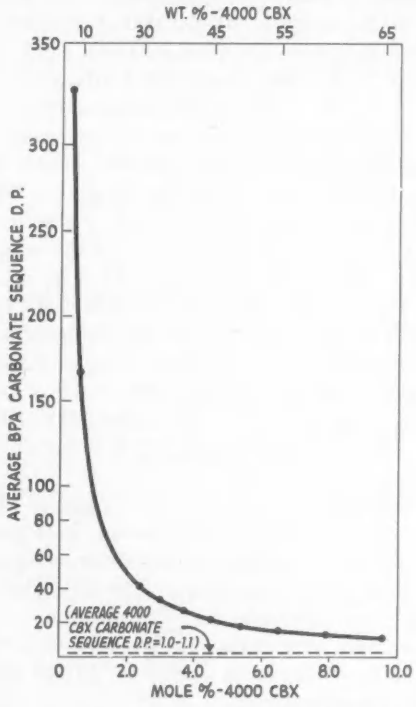


Fig. 3. Change in average bisphenol-A carbonate and 4000 Carbowax carbonate block length in copolymers as a function of composition.

calculated. Thus, for a 4000 Carbowax copolymer, the variation in n and m as a function of composition is depicted in Figure 3. It is apparent that over the composition range considered (0.3–10.0 mole-% 4000 Carbowax) the copolymers have block–block structures in which the polyether carbonate block size remains virtually constant with m = ca. 1.0. However, the bisphenol carbonate block structures, created in satisfying the reaction stoichiometry, vary over a tremendous range of monomer unit D.P. At 0.3 mole-% polyether, for example, n is 333, a block length so large that not more than a single Carbowax molecule could be combined in one polymer molecule. At the other extreme, 9.6 mole-% polyether

requires n to be 10.4, corresponding to a bisphenol carbonate block molecular weight of only ca. 2600. This dramatic 30-fold excursion of aromatic carbonate block size as a function of comonomer mole ratio is clearly a primary factor in explaining the property changes that occur in these and related copolymer systems.

1. Effect of Glycol Molecular Weight

Property–structure effects were first studied by varying Carbowax molecular weight in the range of 1000–20000 at a composition level of 50 wt.-%. Copolymer properties are listed in Table I. It was immediately apparent that with 1000, 4000, and 6000 Carbowaxes, snappy, strong elastomers were produced. Although not accurately measured, the glass transition temperatures for these resins were below room temperature.

The 20000 Carbowax produced only partially soluble resins suggesting crosslinking or extremely high molecular weights. Slight crosslinking due to a polyether hydroxyl functionality slightly greater than two is considered to be the most reasonable explanation for this result.

It is of interest to observe the similar values of T_g exhibited by the 30 wt.-%–20000 CBX copolymer and a 5 wt.-%–4000 CBX copolymer (Table II). The polyether molar concentrations are comparable for these resins. The mole ratio dependence of T_g is further emphasized by comparison of copolymers containing the same weight percentage of polyethers having different molecular weights (T_g = 128°C. for 20000 CBX at 30 wt.-% and 0.4 mole-% vs. T_g = 44°C. for 4000 CBX at 30 wt.-% and 2.4 mole-%).

Thermal-oxidative stability as shown to be poor by substantial 200°C. weight loss in air. Tensile properties, however, were generally excellent. Even at 120°C., the 4000 Carbowax resins retained appreciable strength (2020 psi tensile with 655% elongation). The 1000 Carbowax copolymer showed much poorer hot strength.

Cold-draw orientation of 50–70% was possible, yielding rubbery resins with oriented tensile strengths in excess of 10,000 psi and exhibiting 97–99% immediate elastic recovery.

On the basis of elastic and tensile behavior, the copolymer system derived from the 4000 Carbowax was selected for the further study of the effect of changing composition. This choice was also consistent with the objective of preparing thermoplastic elastomers by drastically dropping T_g and maintaining a high melting point through the use of a reasonably high molecular weight glycol comonomer.

2. Effect of Composition in 4000 Carbowax Copolycarbonate System

The influence of changing composition was investigated for the 4000 molecular weight polyether glycol–bisphenol-A copolycarbonate over a Carbowax composition range of 5–70 wt.-% or 0.3–10.0 mole-%. As shown in Figure 4 both the softening temperature and glass transition

exhibit a linear mole ratio dependence. Figure 4 is in good agreement with data obtained by Coleman[10] for polyether-modified ethylene glycol terephthalate polymers. Most significant is the dramatic sensitivity of

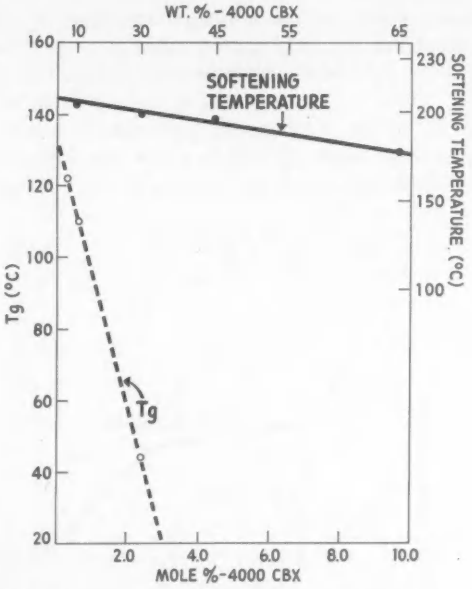


Fig. 4. Effect of composition upon the softening temperature and glass transition of 4000 Carbowax-bisphenol-A copolycarbonates.

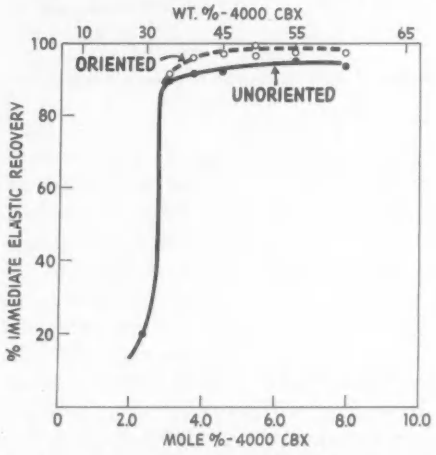


Fig. 5. Change in elastic recovery as a function of 4000 Carbowax-bisphenol-A copolycarbonate composition.

T_g, lowered ca. 100°C. with only a 2.5 mole-% change in composition, and the relative insensitivity of the softening temperature. The T_g passes below room temperature at the 3 mole-% 4000 Carbowax level, and it is at this composition that the polymer changes from a ductile, semirigid material to a snappy elastomer, as indicated in Figure 5. This extremely abrupt effect, occurring over very narrow range of composition, should also be considered in the light of the plummeting bisphenol-A carbonate block length (Fig. 3). This room temperature property transition occurs in the range of D.P. 30–40. Interestingly enough, this corresponds to the molecular weight range (8000–10,000) in which physical properties rapidly mature in the bisphenol carbonate homopolymer. Since the observed

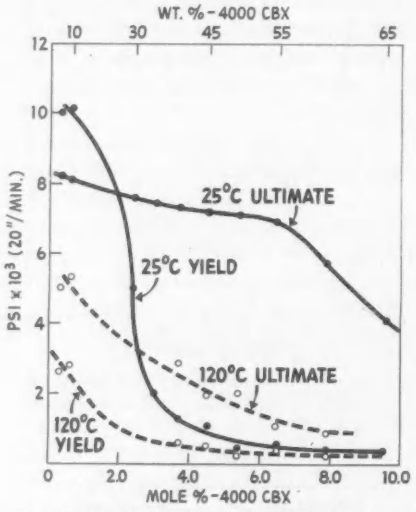


Fig. 6. Tensile properties of 4000 Carbowax–bisphenol-A copolycarbonate as a function of composition.

changes in softening temperature and T_g (and consequently elasticity) depend to a considerable extent upon aromatic carbonate block length, it would be enlightening to determine these properties for aromatic carbonate homopolymers over the molecular weight range 2000–10000 and thereby more accurately judge the contributions of the aromatic polycarbonate and polyether segments to copolymer behavior. Bearing on this point, Merrill[16] has reported a melting point of 185–205°C. for a poly(bisphenol-A carbonate) having an average molecular weight of 1600.

Over the range of composition studied, there is first an increase in stiffness followed by increasing flexibility and finally, above 3 mole-% Carbowax, the onset of strong, snappy rubbery qualities. Tensile properties are impressive (Fig. 6), in that high ultimate tensile strength (7000–8000 psi) is maintained out to ca. 6.5 mole-%. The yield–composition curve of course

drops steeply with the development of elastic properties at 3 mole-%. Tensile strength at 120°C. falls from 5000 to 1000 psi with increasing polyether concentration. Tensile elongation (Fig. 7) increases with increasing Carbowax content from 100% to 700% at 25°C. Exemplary of the remarkable physical properties found in this copolymer system is the 60 wt.-% (7.9 mole-%) copolymer which with orientation displays an ultimate

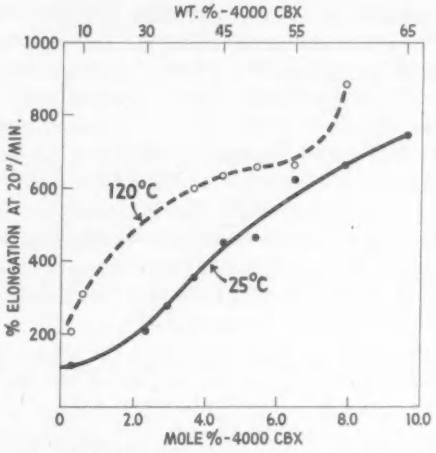


Fig. 7. Tensile elongation of 4000 Carbowax–bisphenol-A copolycarbonate as a function of composition.

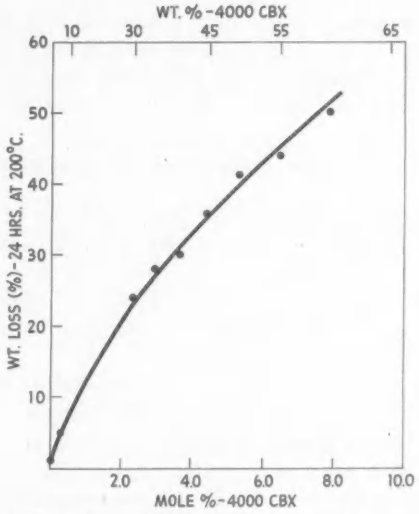


Fig. 8. Thermal-oxidative stability of 4000 Carbowax–bisphenol-A copolycarbonate as a function of composition.

tensile strength of more than 10,000 psi with 405% elongation, 1095 ft.lb./in.^{3} tensile energy, and 97% immediate elastic recovery.

Thermal-oxidative stability was shown to depend upon the polyether concentration (Fig. 8). During a 24 hr. aging period in air at 200°C., the weight loss observed closely corresponded to the poly(oxyethylene) content of the resin. Although the poly(oxyethylene) structure has reasonably good thermal stability, it is known to be quite susceptible to oxidative chain cleavage,[23] presumably by a hydroperoxide decomposition mechanism. The Carbowax copolymer chain might also be cleaved by a carbonate ester pyrolysis leading to an unstable vinyl terminated polyether which would degrade further. That decomposition by ester pyrolysis is at least a contributing factor is suggested by the known formation of propylene during thermal aging of isopropyl-terminated bisphenol-A polycarbonate and by the marked improvement in stability resulting from replacement of carbonate linkages with more pyrolytically stable carboxylate linkages as mentioned in the following section on carbonate–carboxylate polymers.

Addition of antioxidants resulted in improvement in stability as indicated by film aging at 100–150°C. (Table V). However, only a moderate retardation of degradation was accomplished.

As expected, this class of copolymers becomes increasingly hydrophilic with increasing concentration of the polyether linkage. As shown in Table VIII, water absorption at 25°C. is only 0.4% for the 5 wt.-% Carbowax resin, hardly greater than that of the parent aromatic carbonate homopolymer. However, at 30 wt.-%, water absorption increases to 7.8%. At 100°C., almost 16% water is absorbed by this copolymer. Chemical and solvent stability, also listed in Table VIII, are relatively poor, as judged by rapid decomposition in aqueous 10% sodium hydroxide and in 10% sulfuric acid. The polar structure appears to confer appreciable oil resistance. Treatment with 10% nitric acid also produced little change in properties except for a bright yellow coloration of the polymer.

C. Carbonate–Carboxylate Tetrapolymers

The most interesting and unusual characteristics of these polymers were their relatively good thermal-oxidative stability and their unexpectedly low softening temperatures. These tetrapolymers contain four different monomeric structural units: bisphenol-A carbonate (I), 4000 Carbowax carbonate (II), bisphenol-A terephthalate (or other dicarboxylate) (III), and 4000 Carbowax terephthalate (IV).

From the properties listed in Table IV it is apparent that the introduction of isophthalate, terephthalate, or adipate linkages, in partial replacement of the carbonate group, results in a softening point reduction of 100°C. or more, with some resins softening just above room temperature (30–50°C.). This behavior is considered to arise primarily from the disruption of the bisphenol-A carbonate block structure. For structure I, the average D.P. (n) would be 18.5, corresponding to a molecular weight

of 4700, in the absence of isophthalate structures. However, random copolymerization involving 50 mole-% of isophthalate precursor results in a bisphenol-A isophthalate–carbonate copolymer structure in which the average repeat sequences (n and y) are 2.0 for I and III. The block character of the aromatic ester portion of the structure is thereby essentially destroyed resulting in the observed depressing effect upon the softening temperature.

The reason for as much as a 6-fold improvement in thermal-oxidative stability as judged by 200°C. weight loss in air is not well understood. A contributing factor may be the low softening temperature, which at the aging temperature produces a molten sample bead with considerably less surface area than the fluffy, fibrous samples of the higher melting and apparently less stable Carbowax–bisphenol-A copolycarbonates. As mentioned before, another partial explanation may be the replacement of carbonate groups with more pyrolytically stable carboxylate ester groups.

Despite the low softening temperatures, the carbonate–carboxylate tetrapolymers were found to be strong rubbery materials, the terephthalate resin in particular displaying snappy elasticity with 98% recovery.

D. Other Polyether Glycol Copolycarbonates

A number of polyether glycols other than the Carbowaxes were copolymerized at the 50 wt.-% composition level with bisphenol-A. The properties of these resins are summarized in Table III. The Pluronics are hydroxyl-terminated poly(oxyethylene)–poly(oxypropylene) block copolymers available commercially (Wyandotte). Copolymers were somewhat lower melting than the corresponding poly(oxyethylene) resins but a similar high degree of rapid elastic recovery was observed. Thermal-oxidative stability was also comparable to that of the Carbowax copolycarbonates.

Polymeric glycols prepared from propylene oxide, butylene oxide, and styrene oxide (available from Dow) yielded only relatively low molecular weight resins. Although the copolymer from poly(oxybutylene) glycol had an intrinsic viscosity of only 0.26, it was of sufficiently high molecular weight to demonstrate rubbery behavior and appreciable tensile strength (1830 psi). The low degree of polymerization achieved with these glycols was probably caused by chain terminating impurities.

The tetrafunctional Tetronics, containing hydroxyl-terminated poly(oxyethylene–oxypropylene) chains blocked onto ethylenediamine, afforded insoluble rubbery gels as expected and were not further studied.

The author is indebted to J. Mizia for analytical data, E. Powers for assistance with polymerizations and property studies, and Dr. R. W. Kilb for x-ray studies. Permission granted by the General Electric Company for the publication of this paper is also gratefully acknowledged.

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Synopsis

Polycarbonate block copolymers were prepared by phosgenating pyridine solutions of polyether glycol–bisphenol-A mixtures. Copolycarbonates derived from poly(oxyethylene) glycols (Carbowaxes) were studied in detail for property-structure effects as a function of glycol molecular weight (1000–20,000) and copolymer composition (5–70 wt.-% or 0.3–10.0 mole-% of a 4000 molecular weight glycol). Remarkable strength (>7000 psi) and snappy elasticity (>90% immediate recovery) were observed at poly(oxyethylene) block concentrations greater than 3 mole-%. These thermoplastic elastomers also exhibited high softening temperatures (>180°C.) and tensile elongations up to about 700%. Both T_g and softening temperature varied linearly with comonymer mole ratio over the composition range studied, with T_g displaying much greater polyether concentration sensitivity. It is suggested that the observed property effects result to a large extent from the variation in poly(bisphenol-A carbonate) block length that accompanies the changing of copolymer composition. An initial increase in flexural modulus (stiffness) was observed at low polyether concentrations (0–1 mole-%). This phenomenon is considered to be related to similar modulus effects found in plasticized rigid thermoplas-

tics at low plasticizer concentrations. A moderate degree of molecular order, due to bisphenol carbonate segments rather than the normally crystalline polyether, was detected by x-ray analysis. Elastomeric carbonate–carboxylate tetrapolymers were also prepared by partial replacement of carbonate with isophthalate, terephthalate or adipate linkages in polyether-bisphenol systems. The dramatic softening temperature depression observed in this class of polymers is attributed to the disruption of long bisphenol carbonate block sequences that exist in the simpler polyether glycol–bisphenol carbonate copolymers.

Résumé

On a préparé des copolymères à bloc de polycarbonate par phosgénation de solutions pyridiniques d'un mélange de polyéther glycol et de polyéther de bisphénol-A. On a étudié en détail les effets propriétés-structure des polycarbonates dérivés des polyoxyéthylène glycols (carbowaxes) en fonction du poids moléculaire du glycol (1000–20000) et de la composition (5–70% en poids ou 0.3–10% en mole d'un glycol de poids moléculaire de 4000). On a observé une force remarquable (>7000 psi) et une élasticité rapide (cetour à la position initiale immédiate >90%) chez les polyoxyéthylènes en bloc pour des concentrations supérieures à 3 moles %. Ces élastomères thermoplastiques présentent aussi des températures de ramollissement élevées (>180°) et des allongements sous la tension d'environ 700%. Dans le domaine de composition étudié on a observé qu'aussi bien T_g que la température de ramollissement variaient linéairement avec le rapport molaire en commonomère et que T_g présentait une plus grande sensibilité à la concentration en polyéther. On a suggéré que les effets observés résultaient pour une grande part de la variation de la séquence de poly-(bisphénol-A carbonate) qui accompagne le changement de composition du copolymère. On a observé une augmentation initiale du module de flexibilité (rigidité) à de faibles concentrations en polyéther (0–1 mole %). Ce phénomène s'apparente à des effets de module semblables qui ont été observés chez des thermoplastiques rigides plastifiés à faible concentration en plastifiants. Un faible degré d'arrangement a été observé par analyse aux rayons-X; il serait dû plutôt aux segements de carbonate de bisphénol qu'au polyéther habituellement cristallin. Dans les systèmes polymériques d'éther de bisphénol on a remplacé partiellement le carbonate par des ponts d'isophthalate de téréphtalate ou d'adipate et obtenu ainsi des polymères tétrafonctionnels carbonate-carboxylate ayant des propriétés d'élastomères. La diminution dramatique de la température de ramollissement observée dans cette série de polyméres serait due à la rupture des longues séquences de carbonate de bisphénol, qui existent dans les simples copolymères de carbonate de glycol et de bisphénol.

Zusammenfassung

Polycarbonatblockcopolymere wurden durch Phosgenierung einer Pyridinlösung von Polyätherglykol-Bisphenol-A-Mischungen dargestellt. Von Polyoxyäthylenglykolen (Carbowax) abgeleitete Polycarbonate wurden genauer bezüglich des Einflusses der Struktur auf die Eigenschaften in Abhängigkeit vom Molekulargewicht des Glykols (1000–20000) und der Copolymerzusammensetzung (5–70 Gew. % oder 0,3–10,0 Mol % eines Glykols vom Molekulargewicht 4000) untersucht. Bemerkenswerte Festigkeit (>7000 psi) und Elastizität (>90% unmittelbare Rückfederung) wurden bei Polyoxyäthylenblockkonzentrationen grösser als 3 Mol % beobachtet. Diese thermoplastischen Elastomeren besassen auch hohe Erweichungstemperaturen (>180°) und Zugdehnungen bis zu etwa 700%. T_g sowie die Erweichungstemperatur zeigten im untersuchten Zusammensetzungsbereich eine lineare Abhängigkeit vom Comonomerverhältnis, wobei T_g weitaus empfindlicher gegen die Polyätherkonzentration war. Es wird angenommen, dass die beobachtete Beeinflussung der Eigenschaften zum grossen Teil durch die in Begleitung der Copolymerenzusammensetzungs-Änderung auftretende Variierung der Poly(bisphenol-A-carbonat)-Block-länge bedingt ist. Bei niedriger

Polyätherkonzentration (0–1 Mol %) wirde eine anfängliche Zunahme des Biegemoduls (Steifigkeit) beobachtet. Dieses Phänomen scheint zu ähnlichen Moduleffekten bei weichgemachten starren Thermoplasten bei niedriger Weichmacherkonzentration in Beziehung zu stehen. Durch Röntgenanalyse wurde ein mässiger Grad molekularer Ordnung an Stelle des normalen kristallinen Polyäthers festgestellt. Weiters wurden durch teilweisen Ersatz der Carbonat- durch Isophthalat-, Terephthalat- oder Adipatbrücken in Polyäther-Bisphenol-systemen elastomere Carbonat-Carboxylat-Tetrapolymere dargestellt. Die bei dieser Polymerklasse beobachtete starke Herabsetzung der Erweichungstemperatur wird auf die Unterbrechung der langen Bisphenol-Carbonatblocksequenzen zurückgeführt, die in den einfacheren Polyätherglykol-Bisphenolcarbonat-Copolymeren vorhanden sind.

Discussion

E. E. Magat (*Du Pont de Nemours, Wilmington, Del.*): How is the thermal, oxidative, and hydrolytic stability of the carbowax-polycarbonate block copolymers? We have prepared similar block copolymers in the polyethylene terephthate series and found carbowax to confer poor stability.

E. P. Goldberg: The polyoxyethylene linkage confers instability upon aromatic polycarbonates comparable to that observed for your polyethylene terephthalates. The thermal-oxidative stability as measured by weight loss in air at 200° is proportional to the polyoxyethylene content. Additionally, the hydrolytic stability of these block copolymers is poor, probably in large measure due to increased hydrophilicity produced by the more polar polyoxyethylene linkage.

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Polyallomers: Synthesis and Properties

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Introduction

In recent years much research activity has been directed toward the synthesis of crystalline polymers from l-olefins such as ethylene and propylene by means of anionic coordination catalysts. Much of this work has been developmental in nature and has resulted in a number of so-called low pressure processes for the synthesis of polyethylene and polypropylene. At the same time that this work was going forward, considerable work was in progress to determine methods of synthesis and properties of copolymers of ethylene and propylene both with each other and with other vinyl monomers. Rather early in the course of this work it was discovered that random copolymers of ethylene and propylene containing 30–40% propylene possessed elastomeric properties which made them quite useful as synthetic rubbers. Other workers directed their efforts toward the synthesis of block copolymers. Publications in the field of block copolymers prepared by anionic catalysis have appeared from the laboratories of Farbwerke Hoechst,[1,2] Sun Oil Company,[3,4] Montecatini,[5] and Texas Eastman Company.[6]

The purpose of the present paper is to report some of the early work in the Texas Eastman Company Laboratories which led to the commercialization of polyallomers.

Experimental

All of the polymers discussed were synthesized in an 82-gal. stirred autoclave. As a general procedure, a solvent charge of 40 gal. of mineral spirits and a catalyst charge of 57 g. of triethyl aluminum and 51 g. of $TiCl_3$ (aluminum:titanium ratio = 1.5:1) was used. Polymerizations were made at 70–80°C. at a total pressure of 450 psig except where otherwise noted. In most of the runs hydrogen (500 ppm based on the propylene charged) was used to control molecular weight.

The solvent and monomers used were purified by careful fractional distillation and percolation over silica gel.

In those runs where degassing between stages was carried out, the autoclave was vented slowly to atmospheric pressure and dry nitrogen was introduced to 50 psig pressure. The stirrer was then operated for 10 min.

and the vessel was vented to atmospheric pressure. This process was repeated until the vessel had been pressured with nitrogen three times. The second monomer was then introduced to the required pressure and polymerization continued at 70–80°C.

In those cases where the two monomers employed differed widely in polymerization rate as is the case with propylene and ethylene, it is possible to eliminate the degassing step. The least reactive monomer was charged to the autoclave first and polymerization continued to the desired conversion. The more reactive monomer was then added in the required amount and the polymerization completed.

Polymer yields varied from 80 to 120 lb. and reaction times varied from 6 to 12 hr., depending on the nature of the monomers used.

Most runs were worked up by slurrying the crude polymer product in hot isobutyl alcohol several times followed by drying in a double cone rotary vacuum dryer. The polymers were stabilized with 0.1% dilauryl thiodipropionate and 0.1% butylated hydroxytoluene antioxidant. Physical properties were determined on injection molded specimens. Wherever possible, standard ASTM test methods were used.

Ethylene content of the polyallomers was determined by infrared analysis of thin films of polymer with a Perkin-Elmer Model 21 infrared spectrophotometer. The ratio of absorbances at 13.90 and 9.60 μ was compared to a calibration curve prepared using known amounts of linear polyethylene and polypropylene.

Results and Discussion

The term polyallomer is used to identify a new class of polymers synthesized from two or more monomers but exhibiting a degree of crystallinity normally associated only with the l-olefin homopolymers. The word polyallomer is derived from the Greek words *allos*, *meros*, and *poly*. *Allos* means other and denotes a differentiation from the normal. The word *meros* simply means parts. The prefix *poly* is added to show that the new compounds are polymeric. These new polymers are examples of allomerism in polymer chemistry. Allomerism is defined as a constancy of crystalline form with a variation in chemical composition. Polyallomers are crystalline but differ from the commercially available crystalline homopolymers in that they are comprised of two or more monomers and exhibit a superior combination of physical properties.

The polyallomers prepared from propylene and ethylene have quite different properties from blends of polyethylene and polypropylene containing the same proportions of the two monomers. The propylene–ethylene polyallomers are also quite different from the ethylene–propylene rubbers which are presently available commercially. The ethylene–propylene rubbers have properties quite similar to other rubbers in that they have very high elasticity and elongation but very little stiffness, hardness, and tensile strength. Even at molecular weights greater than 100,000 ethylene–

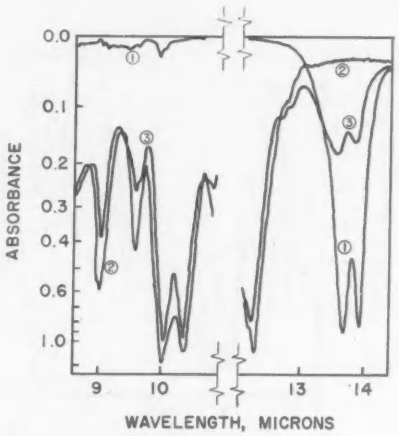

Fig. 1. Infrared curves of (*1*) linear polyethylene, (*2*) polypropylene, (*3*) propylene–ethylene polyallomer.

propylene rubbers are generally 100% soluble in boiling hexane and, therefore, apparently entirely amorphous.

A great deal of experimental evidence has been accumulated to indicate that the polymer chains in polyallomers include homopolymerized segments of each of the monomers employed. Each of these segments exhibits the crystallinity normally associated only with the homopolymers of these monomers. Polyallomers synthesized from propylene and ethylene, for example, are insoluble in hot hexane and heptane, indicating that they are highly crystalline materials. The infrared spectra of the propylene–ethylene polyallomers differ markedly from the spectra of commercially available propylene–ethylene copolymers. In the region 13.7–13.9 μ, linear polyethylene absorbs strongly. Crystalline polypropylene absorbs very little in this region. The polyallomer shows an absorption intermediate between that of linear polyethylene and crystalline polypropylene. Infrared spectra of polypropylene, linear polyethylene, and a propylene–ethylene polyallomer are shown in Figure 1.

Blends of linear polyethylene with crystalline polypropylene show absorbance in the region 13.7–13.9 μ, but the shape of the curve is quite different from that of the polyallomer which has greater absorbance at 13.7 μ. Ethylene–propylene copolymer rubber exhibits a broad, diffuse absorption band in the region 12.5–14.5 μ. The copolymer-rubber spectra also differs from the polyallomer in the region 9.2–9.7 μ. Absorption bands in this area denote crystallinity in polymerized propylene. The polyallomer absorbs strongly in this region whereas the copolymer rubber shows little or no absorbance. Infrared spectra of a linear polyethylene–polypropylene blend, an ethylene–propylene copolymer rubber, and a propylene–ethylene polyallomer are shown in Figure 2.

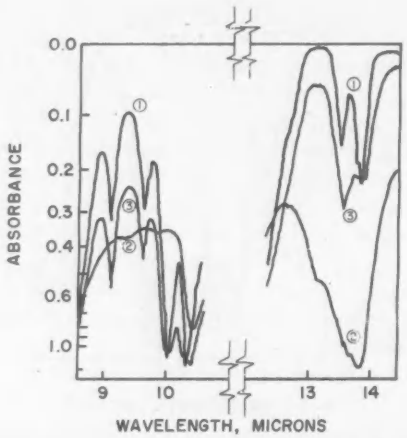

Fig. 2. Infrared curves of (*1*) polypropylene–linear polyethylene blend, (*2*) ethylene–propylene copolymer rubber, (*3*) propylene–ethylene polyallomer.

Other data indicating that the propylene–ethylene polyallomers contain polymer chains comprised of homopolymerized segments of propylene and homopolymerized segments of ethylene include x-ray diffraction data and physical properties. A detailed comparison of physical properties of several propylene–ethylene polyallomers with linear polyethylene, polypropylene, and blends of linear polyethylene with polypropylene is given in the subsequent discussion.

The most interesting features of the propylene–ethylene polyallomers become apparent when their physical properties are compared with those of certain other polyolefins. Table I compares certain properties of propylene–ethylene polyallomers containing 0.6, 2.0, and 3.0% ethylene (Runs 70, 71, and 79) with polypropylene prepared in the experimental unit (Run 11). The procedure used in preparing the polyallomers was the same as that given in the experimental section. After degassing, only the required amount of ethylene was metered in. The pressure during the ethylene polymerization step never exceeded 30 psig, and the reaction was interrupted when the desired ethylene content was reached.

For materials of the same flow rate the density of the polyallomer is less than the density of polypropylene. The brittleness temperature of the polyallomers is sharply reduced when compared with polypropylene. The tensile strength at yield of the polyallomers is less than that of the polypropylene. Elongation of the polyallomers is much greater than that of polypropylene reflecting the high toughness of these materials. Stiffness of the polyallomers is also somewhat less than that of polypropylene. Hardness of the polyallomers is somewhat lower than for polypropylene. Vicat softening point is again lower than for polypropylene. Tensile impact strengths of 56, 79, and 90 ft.-lb./in.^{2} are substantially higher than

TABLE I
Comparison of Properties of Propylene–Ethylene Polyallomers and Polypropylene

	Run 11	Run 70	Run 71	Run 79
Ethylene, %	0.0	0.6	2.0	3.0
Flow rate at 230°C. dg./min.	2.4	2.8	2.9	2.5
Density (annealed), g./ml.	0.9100	0.9093	0.9044	0.9010
Brittleness temperature, °C.	+8	−5	−22	−35
Tensile strength at yield, psi	4700	3870	3560	3050
Elongation, %	360	550	500	>650
Stiffness in flexure, psi	142,000	99,500	92,400	80,000
Hardness, Rockwell R scale	93	87	68	60
Vicat softening point, °C.	145.0	140.3	127.2	124.5
Notched Izod impact strength (23°C), ft.-lb./in.	0.5	0.9	1.9	3.5
Unnotched Izod impact strength (23°C.), ft.-lb./in.	24	No break	No break	No break
Tensile impact strength, ft.-lb./in.^{2}	32	56	79	90

TABLE II
Comparison of Properties of Propylene–Ethylene Polyallomers with Linear Polyethylene

	Run 23	Run 70	Run 71	Run 79
Ethylene, %	100	0.6	2.0	3.0
Flow rate at 230°C., dg./min.	2.4	2.8	2.9	2.5
Density (annealed), g./ml.	0.9724	0.9093	0.9044	0.9010
Brittleness temperature, °C.	<−78	−5	−22	−35
Tensile strength at yield, psi	3100	3870	3560	3050
Elongation, %	290	550	500	>650
Stiffness in flexure, psi	101,000	99,500	92,400	80,000
Hardness, Rockwell R scale	54	87	68	60
Vicat softening point, °C.	122.8	140.3	127.2	124.5
Notched Izod impact strength (23°C), ft.-lb./in.	1.3	0.9	1.9	3.5
Unnotched Izod impact strength (23°C.), ft.-lb./in.	No break	No break	No break	No break
Tensile impact strength, ft.-lb./in.^{2}	63	56	79	90

for polypropylene. The Izod impact strength is also greatly improved for the polyallomers.

In summary, the propylene–ethylene polyallomers overcome the most serious property deficiencies of crystalline polypropylene, offering lower brittleness temperatures, higher impact strengths, and less notch sensitivity. The polyallomers also exhibit the desirable built-in hinge effect that is exhibited by crystalline polypropylene.

A detalled comparison of the propylene–ethylene polyallomers of Table I with an experimental linear polyethylene is given in Table II. The experimental polyethylene was prepared as outlined in the experimental section at an ethylene pressure of 50 psig.

The density of the polyallomers is much lower than the density of the linear polyethylene. The brittleness temperature is not as low but is still adequate for most applications. The tensile strength at yield is about the same for polyallomers as for the polyethylene. Elongation is much higher for the polyallomer. Stiffness in flexure is about the same. The polyallomers are generally superior in hardness, Vicat softening point, tensile impact strength, and Izod impact strength.

The comparison between the linear polyethylene and a polyallomer is continued in Table III.

TABLE III
Comparison of Stress Crack Resistance and Mold Shrinkage of a Propylene–Ethylene Polyallomer and Linear Polyethylene

	Run 23	Run 71
Ethylene, %	100	2.0
Flow rate at 230°C., dg./min.	2.4	2.0
Bell crack test		
100% Igepal	7	0
10% Igepal	4 } Failures at 240 hr.	0 } Failures at 1200 hr.
n-Propanol	0	0
Mold shrinkage, in./in.		
50°C. above cold point	0.032	0.018
100°C. above cold point	0.035	0.019

The Bell crack test utilizing slowly cooled specimens showed no failures at 1200 hr. in any of the test media for the polyallomer sample. The linear polyethylene showed a number of failures at 240 hr. Linear polyethylenes with higher flow rates generally show even less resistance to stress cracking. The superior stress crack resistance of the propylene–ethylene polyallomers is confirmed by storage tests of bottles filled with ammonia and heavy duty detergent. The polyallomer is unaffected, whereas the linear polyethylene bottles were definitely attacked.

Mold shrinkage for the polyallomer is about half that for linear polyethylene. The polyallomer shows almost exactly the same value as polypropylene. This property is of significance in molding operations where a low, uniform mold shrinkage is desirable in order to avoid sinks and warpage in the molded product.

It is of some interest to compare the properties of a typical polyallomer with blends of linear polyethylene and polypropylene. Table IV presents this comparison using Run 71 polyallomer and the experimental polypropylene and linear polyethylene as blend components.

Examination of the data in Table IV indicates that blends of linear polyethylene and polypropylene do not provide the combination of properties that the polyallomer has. Even 25% polyethylene blended into polypropylene reduced the brittleness temperature only to −3°C. Elongation for the blends is little different from that of the polypropylene. Stiffness and tensile strength at yield differ but little from crystalline polypropylene.

TABLE IV
Comparison of Properties of a Propylene–Ethylene Polyallomer and Linear Polyethylene–Polypropylene Blends

		Blends of Run 23 linear polyethylene with Run 11 polypropylene		
	Run 71 polyallomer	5% polyethylene	10% polyethylene	25% polyethylene
Flow rate at 230°C., dg./min.	2.9	1.5	2.5	1.9
Density (annealed), g./ml.	0.9044	0.9132	0.9164	0.9210
Brittleness temperature, °C.	−22	+1	0	−3
Tensile strength at yield, psi	3560	4400	4400	4200
Elongation, %	500	110	200	150
Stiffness in flexure, psi	92,400	134,000	133,000	130,000
Hardness, Rockwell R scale	68	91	88	83
Vicat softening point, °C.	127.2	143.1	139.4	139.1
Notched Izod impact strength (23°C.), ft.-lb./in.	1.9	0.6	0.6	0.7
Unnotched Izod impact strength (23°C.), ft.-lb./in.	No break	No break	No break	No break
Tensile impact strength, ft.-lb./in.^{2}	79	35	38	44

The blends show a gradual decrease in hardness and Vicat softening point with increasing polyethylene content. Tensile impact strength and notched Izod impact strength of polypropylene are improved only slightly by blending with linear polyethylene.

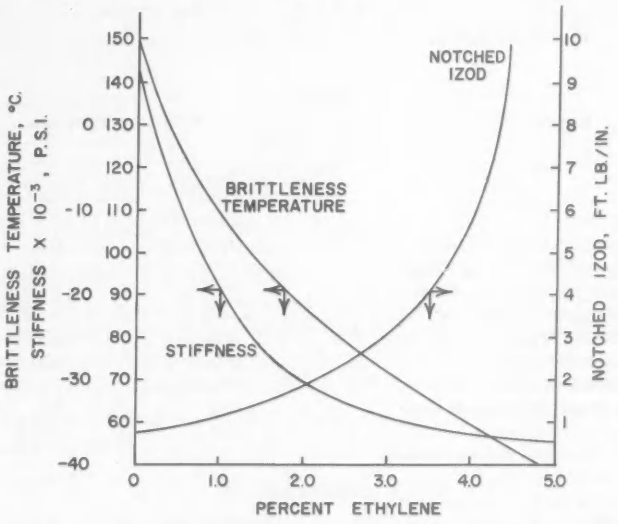

Fig. 3. Effect of ethylene content on brittleness temperature, stiffness, and impact strength of a propylene–ethylene polyallomer.

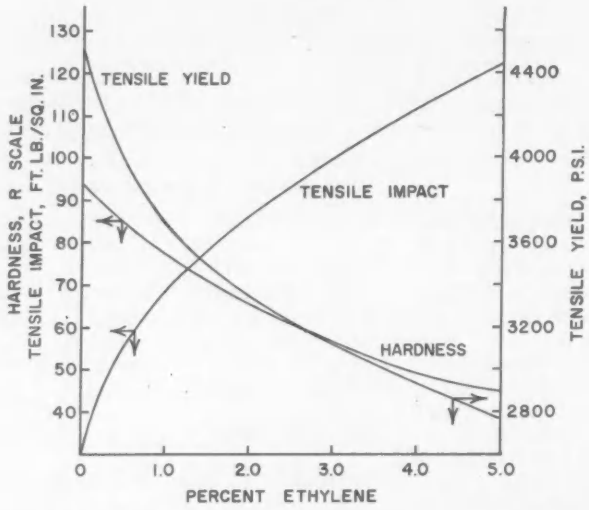

Fig. 4. Effect of ethylene content on hardness, tensile impact, and tensile yield of a propylene–ethylene polyallomer.

Propylene–ethylene polyallomers have been made with brittleness temperatures as low as −50°C. and notched Izod impact strengths well above 10 ft.-lb./in. of notch. Figure 3 shows the effect of ethylene content on stiffness, notched Izod impact strength, and brittleness temperature over the range of ethylene contents of 0–5%. Figure 4 relates tensile strength at yield, tensile impact strength, and hardness to ethylene content. The

TABLE V
Effect of Molecular Weight on Properties of Propylene–Ethylene Polyallomers

	Run 71	Run 114
Ethylene, %	2.0	2.2
Flow rate at 230°C., dg./min.	2.9	0.6
Inherent viscosity in tetralin	1.80	2.38
Density (annealed), g./ml.	0.9044	0.9030
Brittleness temperature, °C.	−22	−32
Tensile strength at yield, psi	3560	3250
Elongation, %	500	600
Stiffness in flexure, psi	92,400	78,800
Hardness, Rockwell R scale	68	64
Vicat softening point, °C.	127.2	128.0
Notched Izod impact strength (23°C.), ft.-lb./in.	1.9	10.8
Unnotched Izod impact strength (23°C.), ft.-lb./in.	No break	No break
Tensile impact strength, ft.-lb./in.^{2}	79	125

data for both Figure 3 and Figure 4 were obtained from polyallomers with flow rates in the range 1.5–3.5.

The effect of molecular weight on the physical properties of propylene–ethylene polyallomers is illustrated in Table V.

In this table a propylene–ethylene polyallomer with an inherent viscosity of 1.80 (run 71) is compared with a propylene–ethylene polyallomer with an inherent viscosity of 2.38 (run 114). It will be noted that the brittleness temperature is lowered and the impact strength is increased, normal results of a large increase in molecular weight.

The excellent toughness of propylene–ethylene polyallomers, as indicated by the low brittleness temperature and high impact strength, is also reflected in the excellent impact strength of polyallomer film. Properties of film made by the chill roll-casting process from two propylene–ethylene polyallomers and an experimental polypropylene are given in Table VI.

TABLE VI
Comparison of Properties of Chill Roll Film from Polypropylene and Propylene–Ethylene Polyallomers

	Propylene–Ethylene Polyallomers		
	Propylene–ethylene Polyallomer, Run 71	Propylene–ethylene Polyallomer, Run 79	Polypropylene, Run 11
Ethylene, %	2.0	3.0	0.0
Film thickness, mils	1.0	1.0	1.0
Transparency, %	70	56	71
Haze, %	1.5	3.2	1.8
Gloss, %	83	80	79
Impact strength (dart weight), g.—			
26 in. drop height	84	110	
13 in. drop height			50

It will be noted that the improved film toughness is gained at little or no expense in optical properties.

The experimental techniques described for sequential polymerization of the monomer pair: propylene–ethylene have been extended to numerous other monomer pairs, notably propylene–butene-1, propylene–butadiene, propylene–styrene, propylene–vinyl chloride, propylene–tetramethylbutadiene and propylene–isoprene. The properties of the resultant polymers cover a very broad range. Detailed analysis of the effect of monomer composition on the physical properties of these polymers will be reported in a later communication.

Conclusions

Propylene–ethylene polyallomers differ markedly in solid-state properties from crystalline polypropylene and linear polyethylene. When compared

to poly-propylene, the propylene–ethylene polyallomers exhibit lower brittleness temperatures, higher impact strength, and less notch sensitivity. When compared to linear polyethylene, the propylene–ethylene polyallomers have lower density, approximately equal stiffness and tensile strength, and have superior hardness, Vicat softening point, and stress crack resistance.

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Synopsis

Description of a new class of highly crystalline stereoregular thermoplastic polymers called "polyallomers." "Allomery" suggests a similarity of crystalline structure with that of polymers with a different chemical composition. For example, polyallomers from ethylene and propene are as crystalline as linear homopolyethylene or homopolypropene. They have the hardness and impact resistance of the first at low temperature, the resistance to failure, film transparency and molding facility of the second, as well as some other peculiar properties. They differ thus considerably by their physical characteristics from the usual elastomers prepared by copolymerization of ethylene and propylene. Polyallomers were prepared from propylene and some other monomers, as ethylenic, acetylenic hydrocarbons or dienes, or several other vinylmonomers. The polymers which were obtained differ considerably from the corresponding homopolymers, their mixtures or the usual copolymers with the same chemical composition. Besides the methods of preparation and the methods of determination of their structure, special attention is devoted to the physical properties of polyallomers derived from propene with ethylene.

Résumé

Une nouvelle classe de polymères thermoplastiques stéréoréguliers, à structure fortement cristalline, pour lesquels on propose le nom de polyallomères est descripte. Le terme "allomérie" suggère une similitude de structure cristalline avec des polymères présentant une composition chimique différente. Par exemple les polyallomères préparés à partir d'éthylène et de propène apparaissent aussi nettement cristallins que l'homopolyéthylène linéaire ou que l'homopolypropène. Ils possèdent la dureté et la résistance au choc à basse température du premier, la résistance à la craquelure, la transparence à l'état de film et la facilité de moulage du second, plus certaines autres propriétés particulières. Ils ne ressemblent donc en rien par leurs caractéristiques physiques aux élastomères habituellement obtenus par copolymérisation d'éthylène et de propène. Des polyallomères ont été préparés à partir de propène d'une part et des monomères choisis dans la gamme des hydrocarbures éthyléniques, diéniques ou acétyléniques,—ou de divers monomères vinyliques—d'autre part. Les produits macromoléculaires obtenus diffèrent là encore, nettement, aussi bien des hompoloymeres correspondants que de leurs mélanges ou des copolymères de même composition préparés par les techniques de polymérisation habituelles. Outre les procédés de préparation et les méthodes utilisées pour l'établissement de la structure, on décrira plus spécialement les propriétés physiques des polyallomères dérivés du propène avec l'éthylène.

Zusammenfassung

Eine neue Klasse thermoplastischer, stereoregulärer Polymerer mit hochgradig kristalliner Struktur wird beschrieben und dafür der Name "Polyallomere" vorgeschlagen. Mit "Allomerie" soll eine Ähnlichkeit der kristallinen Struktur bei Polymeren von verschiedener chemischer Zusammensetzung bezeichnet werden. Zum Beispiel erscheinen die aus Äthylen und Propen dargestellten Polyallomeren ebenso sauber kristallin wie das lineare Homopolyäthylen oder das Homopolypropen. Sie besitzen die Härte und Tieftemperaturschlagfestigkeit des ersteren, die Rissbildungsbeständigkeit, Transparenz im Fimzustand und leichte Verformbarkeit des letzteren und ausserdem gewisse andere besondere Eigenschaften. Sie ähneln daher in ihrer physikalischen Charakteristik in keiner Weise den üblicherweise durch Copolymerisation von Äthylen und Propen erhaltenen Elastomeren. Polyallomere wurden ausgehend von Propen einerseits und von ausgewählten Monomeren aus dem Bereich der Äthylen-, Dien- oder Acetylenkohlenwasserstoffe—oder verschiedenen Vinylmonomeren—andererseits dargestellt. Die erhaltenen makromolekularen Produkte unterscheiden sich sowohl von den entsprechenden Homopolymeren als auch von ihren Mischungen oder von den nach den üblichen Polymerisationsverfahren dargestellten Copolymeren gleicher Zusammensetzung. Ausser dem Darstellungsprozess und den zur Strukturermittlung angewendeten Methoden, werden eingehend die physikalischen Eigenschaften der Polyallomeren aus Propylen und Äthylen sind im einzelnen beschrieben.

Discussion

A. Nicco (*Ethylène Plastique, Lens, France*): D'après la conférence de M. Coover sur divers systèmes catalytiques du type employé pour effectuer la polymérisation, la durée de formation d'une macromolécule (durée de vie) serait très courte (1 M_n); or pour obtenir des copolymères à blocs suivant le procédé décrit il faut une durée die vie de plusieurs dizaines de minutes au moins, ce qui paraît contradictoire.

J. P. Dubosc (*Kodak Pathé, France; presenting the paper of H. J. Hagemeyer*): Il n'y a aucun désaccord entre les résutats présentés ici et ceux indiqués par le Docteur Coover dans sa conférence générale. En effet, cet auteur a montré que la durée die vie d'une chaîne de polymère en croissance était très courte pour les très faibles taux de conversion. En outre, il a indiqué que, pour des taux de conversion supérieurs à 2 grammes de polymère par gramme de trichlorure de titane, la proportion effective de transfert de chaîne est considérablement élevée, ce qui a pour résultat d'augmenter la durée de vie des chaînes croissantes. Dans le cas des polyallomères, le taux de conversion par gramme d'halogénure de titane est nettement supérieur à la limite indiquée ci-dessus et des durées de vie de 5 à 6 jours ont été couramment observées. Des constatations similaires pour les taux de conversion élevés ont été indiquées par Kontos et al. (*J. Polymer Sci.*, **61**, 69–82 (1962)) et Bier et al. (*Makromol. Chem.*, **44–46**, 347–357 (1961)).

P. Pino (*Pisa, Italy*): (*1*) Do you have any data on the fractionation of polyallomers by solvent extraction?

(*2*) On what basis can you exclude on the presence of polypropylene homopolymer in the polyallomers?

J. P. Dubosc: (*1*) Solvent fractionation of polyallomers indicates the composition to be fairly uniform for the entire molecular weight range.

(*2*) The presence of any appreciable quantity of homopolymeric polypropylene in the polyallomer is excluded on the basis of fractionation and by the low temperature and impact properties for a given ethylene concentration.

G. Bo (*Sté Rhône-Poulenc, Lyon, France*): Vous avez montré des spectres I. R. d'élastomère éthylène-propylène et de polyallomère. Or les élastomères éthylène-propylène contiennent 40–50% d'éthylène, alors que les polyallomères n'en contiennent que 2–3%. La comparaison me semble donc difficile et je voudrais savoir si vous avez enregistré

des spectres avec un copolymère à 2 ou 3% d'éthylène préparé par simple copolymérisation et si non, quelle différence vous avez remarqué entre ce spectre et celui d'un poly allomère?

J. P. Dubosc: L'allure des courbes d'absorption dans l'infra-rouge des copolymères propène-éthylène est indépendante de la concentration de chacun des monomères. L'absorption augmente avec la proportion d'éthylène dans le copolymère, mais les formes des courbes et les zones d'absorption ne changent pas, ce qui nécessite seulement d'utiliser un échantillon moins épais pour les fortes teneurs en éthylène. Par usite, les différences observées dans les spectres d'absorption dans les domaines 9–10 μ et 13–14 μ, et indiquées dans la Figure 3, sont caractéristiques de la différence de structures existant entre les copolymères propène-éthylène et les polyallomères préparés à partir des deux mêmes monomères.

L. S. Rayner (*I. C. I. Ltd. Herts, Great Britain*): Have you compared the properties of your polyallomers with those of polypropylene blended with rubbers such as polyisobutylene or ethylene-propylene rubber?

J. P. Dubosc: Some properties of the polyallomers are quite similar to the rubber-modified polypropylenes. However, the polyallomers are superior with respect to color, clarity, moldability, and resistance to blushing when bent or stretched. The polyallomers have excellent optical properties in cast and biaxially oriented films, whereas the rubber-modified polypropylenes are completely unsatisfactory because of the nonhomogeneity of the blend.

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Polyester–Urethane Block Terpolymers

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INTRODUCTION

Although the preparation of block copolymer polyurethanes[1–3] has been reported, the synthesis and properties of terpolymer polyurethanes designed from three different polyesters have not been investigated. Previous work has shown[2] that block copolymer polyester–urethanes containing 15–30% terephthalate show improved tensile strength as well as elasticity and solvent resistance. This paper is concerned with terpolymer polyurethanes prepared from three polyesters with the aim of improving tensile strength, per cent elongation, solvent resistance, and heat stability. Polyurethanes were prepared by chain extending different ratios of poly(1,4-butylene adipate), poly(1,5-amylene isophthalate), and poly(ethylene isophthalate) hydroxyl number = 90 ± 5) with methylene bis(4-phenyl isocyanate). After an optimum ratio of polyesters was established, the molecular weight of the isophthalate polyesters was varied to determine the effect of molecular weight upon physical properties. A comparison of physical properties of block terpolymers and completely random polymers was also made.

EXPERIMENTAL

Materials

Methylene bis(4-phenyl isocyanate) was purified by distillation, boiling point 186°C./2 mm. Ethylene glycol, 1,4-butanediol, and 1,5-amylene glycol were distilled before use. Adipic acid and isophthalic acid (melting points 151–153°C. and 340–342°C., respectively) were used without further purification.

Preparation of Polyesters

The polyesters were prepared in a three-necked flask fitted with a modified Dean-Stark trap and condenser, a thermometer, and a nitrogen inlet tube. In general, 1 mole of acid, 2.0 moles of glycol, and a catalytic amount of yellow lead oxide were heated in a nitrogen atmosphere at 160–180°C. until the polyester had an acid number of 0–2. The excess glycol was then removed *in vacuo* to obtain the desired hydroxyl number. The

molecular weights of these polyesters were calculated from results of end-group analysis. The hydroxyl endgroups were determined by acetylation with pyridine–acetic anhydride reagent.[4,5] The carboxyl endgroups were titrated directly in acetone or pyridine–acetone solution with 0.1*N* sodium hydroxide.

In the case of a completely random polyester, the ratio of glycol to acid was calculated to give the desired hydroxyl number (see Table VII).

Preparation of Block Terpolymers

The polyester–urethane block terpolymers were prepared in bulk as follows. The polyesters were weighed in a glass jar and made homogeneous by melting at 110–150°C. The reaction mixture was cooled to 120°C. and an equivalent amount of methylene bis(4-phenyl isocyanate) added with constant stirring. The mixture became too thick to stir after 1 min. and was capped and placed in an oven at 110°C. for 2.5 hr. At the end of this time the samples were cooled and removed from the jar. The reaction products which usually contained entrapped air were molded into test pieces in a 4-in. slab mold at 205°C. at 1600 psi. Tensile specimens were aged two weeks before testing.

DISCUSSION AND RESULTS

This investigation was concerned with the preparation of a series of thermoplastic polyester–urethanes prepared by chain extending a mixture of poly(1,4-butylene adipate) (PBA), poly(ethylene isophthalate) (PEI), and poly(1,5-amylene isophthalate) (PAI) with methylene bis(4-phenyl isocyanate). In order to ascertain the optimum ranges, a series of samples was prepared with varying percentages of PBA. Table I shows that elastomeric terpolymer polyurethanes may be prepared with as much as 75% isophthalate providing the polyisophthalates in the composition are present in approximately 1:1 ratio. These data show that Sample 3 which has a per cent composition of 40% PBA/10% PAI/50% PEI possesses the best tensile and per cent elongation.

In order to demonstrate that the bulk polymerization method was not causing transesterification to give completely random copolymers, two random copolymers were made up using this model where (*1*) a completely random polyester (hydroxyl number = 90 ± 5) was made up from isophthalic acid, adipic acid, 1,4-butanediol, 1,5-amylene glycol, and ethylene glycol, and chain extended with methylene bis(4-phenyl isocyanate), and (*2*) a random polyester was made up from isophthalic acid, 1,5-amylene glycol and ethylene glycol (hydroxyl number = 90 ± 5). A mixture of this polyester (60%) and PBA (40%) was chain extended with methylene bis(4-phenyl isocyanate). Table II is a summary of these data.

It was desired to know the effects of changing the molecular weight of the isophthalates using the model (Table I, Sample 3). Table III is a summary of the data obtained when the molecular weights were varied.

TABLE I
Physical Properties of Polyurethanes (Polyester $\bar{M}_n \simeq 1200$)

Sample	PBA, %[b]	PAI, %[c]	PEI, %[d]	Tensile, psi	Elongation, %	Wallace hardness	(η)[a]
1	60	20	20	Too soft to test			
2	50	10	40	4890	570	55	0.55
3	40	10	50	6490	460	62	0.71
4	40	20	40	6170	480	60	0.61
5	40	30	30	5670	530	54	0.50
6	40	40	20	3300	560	47	0.49
7	30	10	60	3800	10	86	0.57
8	30	20	50	4050	440	66	0.54
9	30	30	40	3060	490	62	0.37
10	30	40	30	2930	470	57	0.54
11	30	50	20	5090	470	55	0.55
12	25	50	25	3100	490	69	0.46
13	25	40	35	3370	440	66	0.65
14	20	40	40	4190	20	89	0.58

[a] All viscosity data were obtained at 25°C. using dimethylformamide solvent.
[b] $\bar{M}_n$ of PBA was 1188.
[c] $\bar{M}_n$ of PAI was 1332.
[d] $\bar{M}_n$ of PEI was 1290.

TABLE II
Physical Properties of Random and Block Terpolymer Polyurethanes
(Polyester $\bar{M}_n \cong 1200$)

Polyurethane	Tensile, psi	Elongation, %	Wallace hardness	(η)
Block terpolymer[a]	6490	460	62	0.71
Partially random[b]	4010	400	69	0.62
Completely random[c]	2780	550	53	0.45

[a] Block terpolymer prepared by chain extending a polyester mixture of mole-% composition = 40 PBA, 10 PAI, 50 PEI.
[b] Partially random copolymer prepared by chain extending two polyesters: (*1*) 40% PBA and (*2*) 60% of an amylene, ethylene, isophthalate polyester where ethylene glycol: 1,5-amylene glycol = 5:1.
[c] Completely random polyurethane prepared by chain extending a random polyester of adipic acid, isophthalic acid, ethylene glycol, 1,4-butylene glycol, and 1,5-amylene glycol calculated to give the equivalent mole per cent composition of the block terpolymer.

This caused drastic changes in the tensile strength and hardness of the samples.

Further work was done to optimize the physical properties by varying the per cent compositions of the polyesters. Table IV is a summary of these data.

The results of this study have shown that block terpolymers can be prepared with a wide variety of physical properties. The molecular

TABLE III
Physical Properties of Polyurethane (Mole-% Composition = 40 PBA, 10 PAI, 50 PEI) of Varying Polyester $\bar{M}_n$

$\bar{M}_n$ of polyesters			Tensile,	Elongation,	Wallace	
PBA	PAI	PEI	psi	%	hardness	(η)
1188	588	599	5690	580	50	0.56
1188	1332	1290	6490	460	62	0.71
1188	1924	2120	3230	450	86	0.52

TABLE IV
Physical Properties of Terpolymer Polyurethanes where $\bar{M}_n$ of Isophthalate Polyester Was Varied

Sample	Isophthalate M_n range	Adipate $\bar{M}_n$ range	PBA, %	PAI, %	PEI, %	Tensile, psi	Elongation, %	Wallace hardness	(η)
1	600	1200	40	10	50	5690	580	50	0.56
2	600	1200	40	20	40	6480	530	57	0.68
3	600	1200	40	30	30	3490	650	53	0.66
4	600	1200	30	10	60	3500	400	77	0.76
5	600	1200	30	20	50	5170	460	68	0.58
6	600	1200	30	35	35	3400	290	66	0.90
7	600	1200	30	50	20	7530	460	59	0.64
8	600	1200	20	30	50	4970	10	94	0.87
9	2000	1200	60	10	30	3310	570	52	0.76
10	2000	1200	60	20	20	1990	600	48	0.63
11	2000	1200	50	10	40	2770	570	46	0.45
12	2000	1200	50	25	25	5440	510	60	0.52
13	2000	1200	50	40	10	1590	590	51	0.76
14	2000	1200	40	10	50	3240	450	86	0.52
15	2000	1200	40	20	40	3230	430	68	0.61
16	2000	1200	35	15	50	4190	450	62	0.48

weight of these polyesters has a profound effect on the properties of the polyurethanes. Samples of the highest tensile strength were obtained when isophthalate polyester of molecular weights of 600 were used, although polyurethanes of somewhat less tensile strength could be produced from polyesters of 1200 and 2000 molecular weight by changing the proportions of polyesters. It was not possible to relate tensile strength to per cent composition in this study except in the case of the four polymers shown in Figure 1. Other groups of polymers (e.g., 4, 5, 6, and 7 as well as samples 11, 12, and 13 in Table IV) show maxima and/or minima for plots of tensile strength vs. per cent composition.

Low temperature embrittlement of the terpolymer polyester–urethanes were investigated using the Clash-Berg torsion test method (Table V) (ASTM D-1043-51).

In general, the highest values found for low temperature inflexibility were encountered with the 2000 molecular weight polyesters. In addition,

TABLE V
Clash-Berg Torsion Test

$\bar{M}_n$ range	PBA, %	PAI, %	PEI, %	Inflexibility point, (°C.)
600	40	10	50	−16.9
600	40	20	40	−18.9
1200	40	10	50	−10.1
1200	40	20	40	−17.6
1200	40	30	30	−30.4
1200	40	40	20	−25.9
2000	40	10	50	+ 8.2
2000	50	10	40	−13.5

it was found that for a series of samples with PBA constant, inflexibility temperature increased with increasing concentration of PEI or PAI and a greater effect when PEI > PAI. However, it is possible to obtain a minimum temperature in the inflexibility measurement by adjusting the isophthalate concentration to have equal amounts of PEI and PAI.

The solvent resistance of several of the prepared polyurethanes was determined in several solvents to ascertain what differences existed in the terpolymers with respect to chain length and per cent composition. The test was conducted by placing a polyurethane sample of approximately 0.2 g. in a capped bottle containing 10 ml. of solvent. They were left standing at room temperature with occasional shaking for 24 hr. It was found that terpolymer polyurethanes derived from 2000 molecular weight polyesters were more solvent resistant than any of the others (See Table VI).

X-ray powder patterns were run in an effort to determine the effect of the per cent crystallinity on the physical properties. In view of the fact

TABLE VI
Solubility Data[a]

Isophthalate M_n range	PBA, %	PAI, %	PEI, %	Dimethylformamide	Nitrobenzene	2-Butanone	Toluene	Ethyl alcohol
600	40	10	50	1	1	3	4	4
600	30	10	60	1	1	3	4	4
1200	20	40	40	1	1	4	4	4
1200	40	20	40	1	1	2	2	4
1200	30	50	20	1	1	1	2	4
1200	40	10	50	1	1	1	4	4
1200	10	70	20	1	1	1	2	4
1200	40	30	30	1	1	1	2	4
1200	40	40	20	1	1	1	2	4
2000	40	10	50	4	4	3	4	4
2000	60	10	30	3	1	2	2	4

[a] (1) = soluble; (2) = swells; (3) = precipitates; (4) = insoluble.

that all of the materials were elastomeric it was anticipated that they would have rather small amounts of crystallinity. Indeed, this was found to be the case. However, it was not possible to relate the presence or absence of crystallinity to tensile strength measurements.

The data on random copolymers show that the tensile strength decreases as the molecular weight of the polyesters increase. The tensile

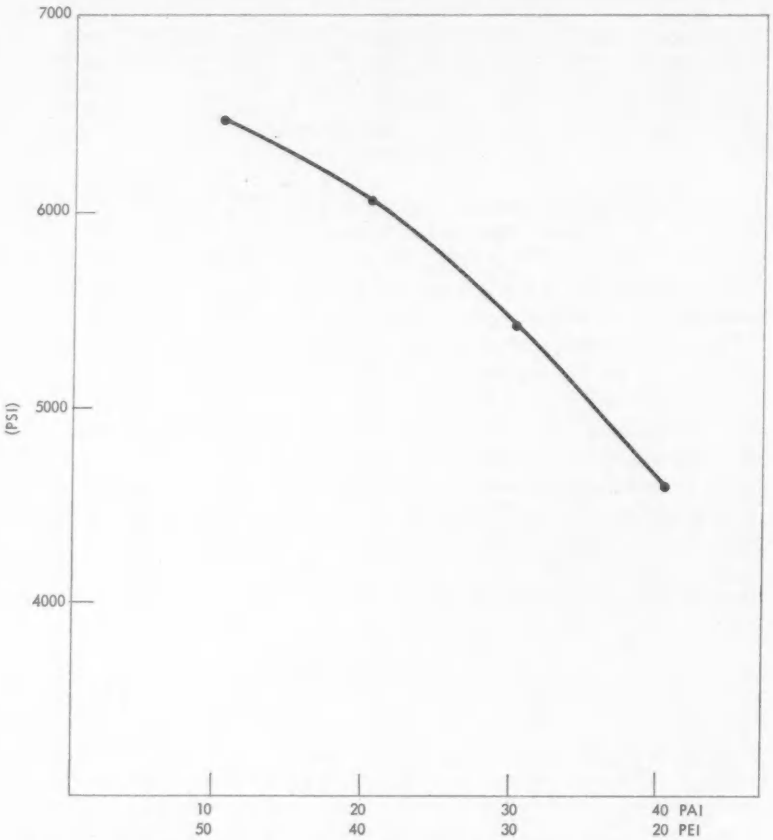

Fig. 1. Tensile strength of polyurethanes ($\bar{M}_n$ = 1200), PBA = 40%; variable PAI and PEI.

strength (10,270 psi) of the polyurethane derived from the lowest molecular weight (553) paritally random isophthalate polyester is almost twice that of the block terpolymer of the corresponding molecular weight (compare Sample 1, Table III to Sample 1, Table VII). By comparing the tensile strengths and intrinsic viscosities of the polymers in Tables I and IV, it can be seen that tensile strength was independent of molecular weight.

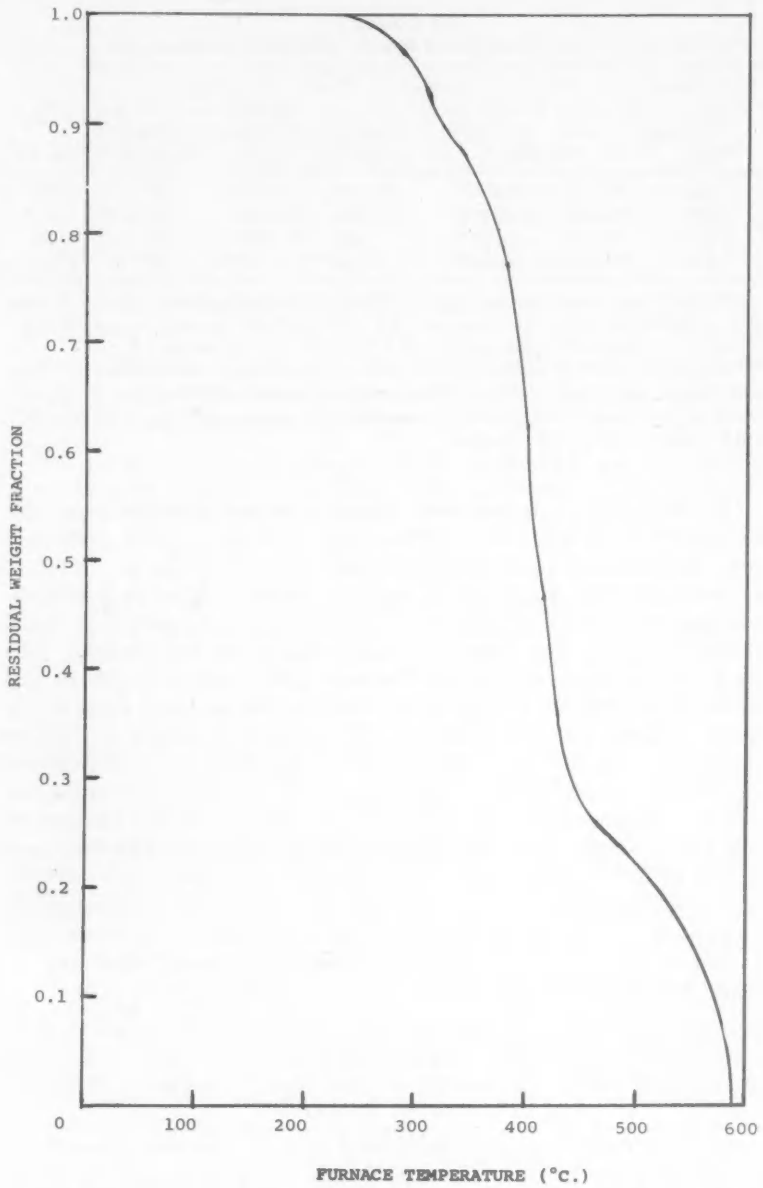

Fig. 2. TGA thermogram of terpolymer polyurethane (composition: 40 mole-% PBA, 10 mole-% PAI, 50 mole-% PEI).

TABLE VII
Physical Properties of Random Polyester–Urethanes

Isophthalate $\bar{M}_n$ range	Polyester	Tensile, psi	Elongation, %	Wallace hardness	(η)
553	Partially random[a]	10,270	510	62	0.80
1180	Partially random[a]	4,010	400	69	0.62
2480	Partially random[a]	1,900	430	81	0.26
1138	Completely random[b]	2,780	550	53	0.45

[a] Partially random means that the block copolymer was prepared by chain extending two polyesters (*1*) 40% PBA of $\bar{M}_n$ = 1188 and (*2*) 60% of an amylene, ethylene isophthalate polyester where ethylene glycol:1,5-amylene glycol ratio is 5:1.

[b] Completely random means that the random polyurethane was prepared by chain extending a random polyester of adipic acid, isophthalic acid, ethylene glycol, 1,4-butylene glycol and 1,5-amylene glycol calculated to give a ratio equivalent to a 40% PBA/10% PAI/50% PEI polymer.

The heat stability of the block terpolymers was investigated by two different approaches. Thermogravimetric analysis[6] (TGA) performed on a typical sample in air using a heating rate of 5°C./min. gave an ipdT of 398°C. (see Fig. 2). However, since this is an empirical method of obtaining a decomposition temperature and gives no information as to the mechanism of decomposition, heat aging data were also obtained. The sample of the same composition was heat aged at 250°C. for 20, 40, and 60 min. time intervals. Table VIII shows the results of heat aging on the smear temperature of the polymers. These data show that the melting point of samples decreased with increasing time at elevated temperatures up to 40 min. Additional heat aging produced samples which merely became friable when heated up to 250°C. It was observed that the samples lost <10% weight under these conditions and that the materials heat aged at 250°C. for 1 hr. were insoluble in dimethylformamide (DMF)-solvent. The infrared spectra of the samples was also obtained by evaporating the chloroform soluble solution of a sample on a salt plate. The absorbances of NH and CH bands listed in Table IX show diminished NH absorption as the time at 250°C. is increased.

TABLE VIII
Heat-Aging Data on Terpolymer Polyurethane (Mole-% Composition = 40 PBA, 10 PAI, 50 PEI)

Time at 250°C., min.	Weight loss, %	Smear temperature, °C.
0	0	144–152
20	2.3	85–93
40	4.6	81–84
60	5.8	[a]

[a] Sample would not smear up to 250°C.

TABLE IX
Infrared Data on Heat Aged Terpolymer Polyurethane (Mole-% Composition = 40 PBA, 10 PAI, 50 PEI)

Time at 250°C., min.	N–H absorbance	C–H absorbance	Ab_{NH}/Ab_{CH}
0	0.220	0.308	0.715
20	0.355	0.563	0.631
40	0.246	0.479	0.514
60	0.130	0.289	0.458

These data along with the solubility data would seem to indicate that crosslinking had occurred through the (—NH) group, giving rise to allophonate linkages. The results of this work show that heating the polymer had not just caused a reorganization to a random copolymer but had actually resulted in a crosslinked material.

The authors are indebted to Messrs. L. Marlin and D. Robertson of the Polymers Department for the physical testing and to Messrs. T. Morgan and J. Montgomery of the Chemistry Department for the viscosity measurements.

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Synopsis

A series of block and random polyester–urethane terpolymers was prepared from poly(1,5-amylene isophthalate), poly(ethylene isophthalate), poly(1,4-butylene adipate) and 4,4′-diphenylmethane diisocyanate. It was found that polyurethanes could be prepared with relatively high concentrations of poly(alkylene isophthalates) with good elasticity. A comparison has been made of the physical properties of these polymers including solvent resistance, tensile strength, elasticity, hardness, low temperature embrittlement, and heat stability. The effects of varying molecular weight and composition of polyester mixtures of block and random polyurethanes were correlated with these physical properties. It was shown that heat aging these terpolymers caused reorganization of their structures via crosslinking reactions which distinctly changed their physical properties.

Résumé

Une série de polymère ternaires polyester–uréthanne séquencés et statistiques a été préparé au départ de polyisophthalate d'amylène 1.5, polyisophthalate d'éthylène, polyadipate de butylène 1.4 et de diisocyanate de 4.4′ diphényle. On peut ainsi préparer des polyréthannes de bonne élasticité contenant une concentration relativement élevée de polyisophthalate d'alcoylène. Les propriétés physiques de des polymères ont été comparées du point de vue résistance aux solvants, force à la tension, élasticité, dureté,

fragilité à basse température, stabilité à la chaleur. Les effets des variations du poids moléculaire et de la composition des mélanges de polyesters des polyuréthannes régénérées et statistiques ont été reliés aux propriétés physiques. Le vieillissement thermique de ces polymères ternaires cause une réorganisation de leurs structures par suite de réactions de pontage qui modifient notablement leurs propriétés physiques.

Zusammenfassung

Eine Reihe von Block- und von statistischen Polyesterurethanterpolymeren wurde aus Poly(1,5-amylenisophthalat), Poly(äthylenisophthalat), Poly(1,4-butylenadipat) und 4,4′-Diphenylmethandiisocyanat dargestellt. Es konnten Polyurethane mit verhältnismassig hoher Konzentration an Poly(alkylenisophthalat) mit befriedigender Elastizität gewonnen werden. Ein Vergleich der physikalischen Eigenschaften dieser Polymeren, nämlich der Lösungsmittelbeständigkeit, Zugfestigkeit, Elastizität, Härte, Tieftemperaturversprödung und Hitzebeständigkeit wurde durchgeführt. Der Einfluss des Molekulargewichts und der Zusammensetzung der Polyestermischungen von Block- und statistischen Polyurethanen wurde zu diesen physikalischen Eigenschaften in Korrelation gesetzt. Hitzealterung dieser Terpolymeren führte über Vernetzungsreaktionen zu einer Umbildung ihrer Struktur, die ihre physikalischen Eigenschaften deutlich änderte.

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Grafting as a Method of Surface Modification of Heterochain Polymers

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The preparation of graft copolymers is a domain of polymerization chemistry that has recently received considerable attention. One of promising developments in this field involves the surface modification of heterochain polymers by grafting. This report deals with some results of our work in this line.

We have previously reported on our investigation of grafting of vinyl monomers on the surface of such heterochain polymers as polyamides, polyesters, and natural fibers, taken as fibers or films.[1–10]

Recently we have also noted the marked effect of the time of ozonization of the initial polymers on the consequent development of the graft polymerization reaction.[2–5]

Our systematic data obtained with polyamides and polyethylene terephthalate revealed a direct dependence of the graft layer yield on the time of the polymer activation with ozone, as shown in Figures 1 and 2.

It has also been found that the ozonization of polymers, even if of short duration, is always accompanied by their partial destruction. This is shown in Figures 3 and 4 which show the changing viscosity of cresol solutions of Lavsan (polyethylene terephthalate) and the varying strength of polyamide films depending on the time of ozonization. Further investigation of the ozonization reaction of some polymers has shown this process to involve a complex of several concurrent oxidation reactions.

Primary oxidation products of polymers are those containing active oxygen. Figure 5 shows the dependence of the formation of such compounds on the time of ozonation of Lavsan. At the same time there are formed products of continued oxidation of polymers that are of acidic character.

The reaction has been studied in more detail with ethylene glycol dibenzoate and ϵ-caprolactam. Figures 6 and 7 show the changing percentage of active oxygen and acidity during the ozonization of these compounds.

It has been thus proved experimentally that the activation of polymers with ozone consists in the primary formation of compounds with active

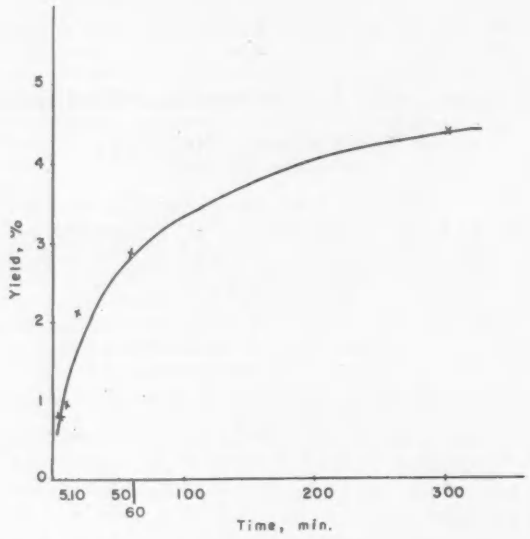


Fig. 1. Dependence of yield of polystyrene grafted to Capron film on the time of ozonization.

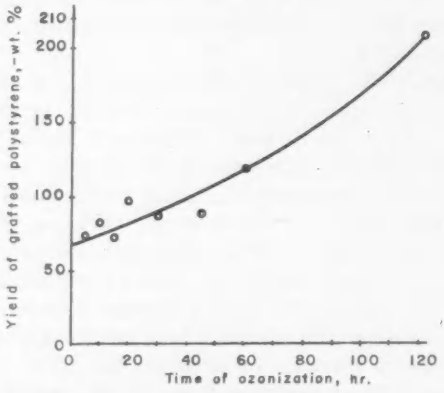


Fig. 2. Dependence of the yield of polystyrene grafted to Lavsan (polyethylene terephthalate) on the time of ozonization.

oxygen that subsequently act as initiators of the graft copolymerization reaction.

As even a short action of ozone causes the destruction of polymers we have made use of a milder oxidant, heated air.[6]

Figure 8 lists experimental evidence, obtained on grafting styrene to polyethylene terephthalate (Lavsan) using heated air as a catalyst.[11]

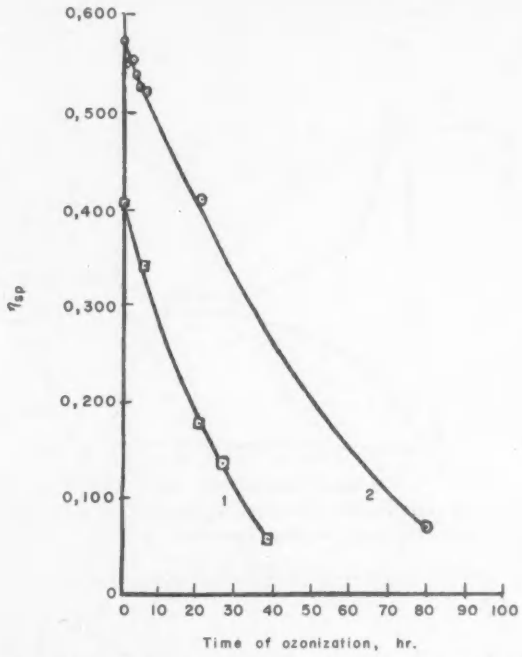


Fig. 3. Dependence of the change in viscosity of polyethylene terephthalate on the time of ozonization: (1) film thickness $\delta = 12\ \mu$; (2) film thickness $\delta = 28\ \mu$.

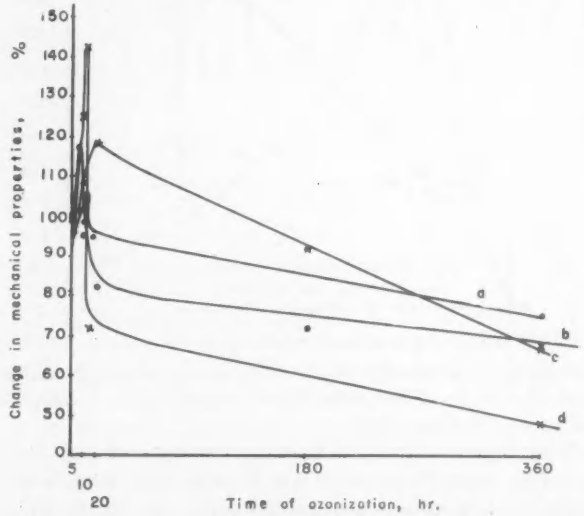


Fig. 4. Dependence of mechanical properties of grafted copolymers of Capron and polyamide or Anide G-669 with styrene on the time of ozonation: (*a*) tensile strength of polyamide graft copolymer; (*b*) tensile strength of capron graft copolymer; (*c*) elongation of Capron graft copolymer; (*d*) elongation of polyamide graft copolymer.

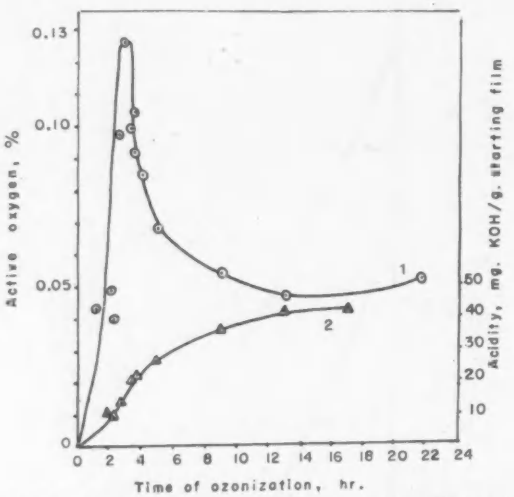


Fig. 5. Change in the percentage of (*1*) active oxygen and (*2*) acidity of the film from polyethylene terephthalate ($\delta = 28\ \mu$) depending on the time of ozonization.

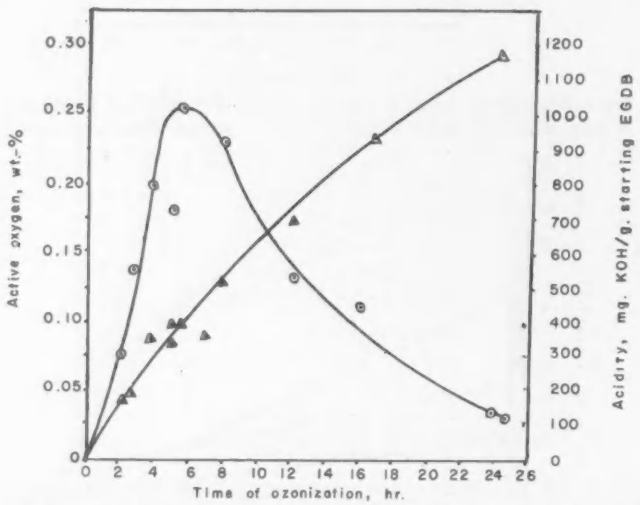


Fig. 6. Change in the percentage of (*1*) active oxygen and (*2*) acidity in the ozonization products of ethylene glycol dibenzoate (EGDB) depending on the time of ozonization.

Comparing these results with those previously obtained[8] for polyamide fibers given in Figure 9 it can be readily seen that there exists a definite optimum of the time of activation of polymers with heated air.

Similar data were found on activating wool and silk with heated air followed by the grafting of acrylonitrile, as shown in Figure 10.[12,13]

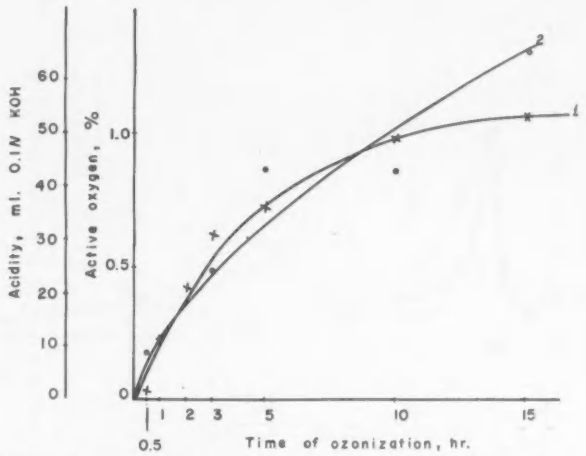


Fig. 7. Change in the percentage of (*1*) active oxygen and (*2*) acidity of ε-caprolactam depending on the time of ozonization.

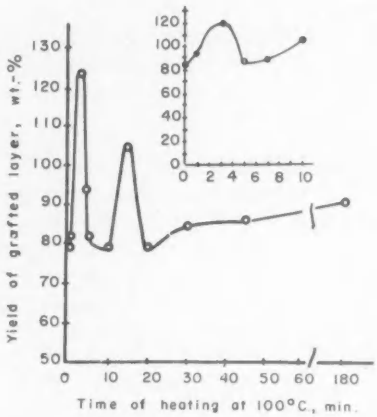


Fig. 8. The effect of the time of thermal treatment at 100°C. on the process of grafting styrene to polyethylene terephthalate.

One could have supposed that short exposure to heated air should give rise in polymers to maximum active centers to initiate the graft copolymerization reactions. However, the search for free radicals and groups containing active oxygen (in polymers) by ESR and infrared spectrometry as well as by analytical methods met with failure On the other hand, the film from polyethylene terephthalate when exposed to air heated to 80°C. was found to reveal increased absorption in the ultraviolet region of the spectrum characteristic of CO compounds (30–33 cm.$^{-1}$). This was accompanied by a decrease in hydrogen (by 0.5%). Figure 11 gives the

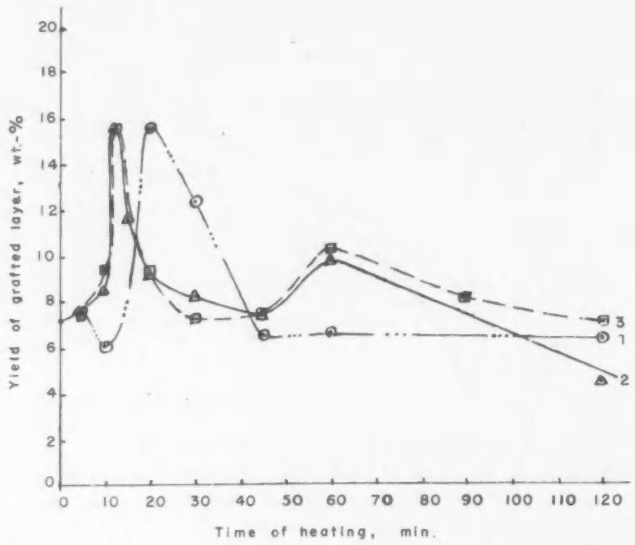


Fig. 9. Effect of the time of thermal treatment at 80–90°C. on the grafting of styrene to nonoriented Capron fiber: (*1*) at 80°C. in nitrogen; (*2*) at 80°C. in air; (*3*) at 90°C. in air.

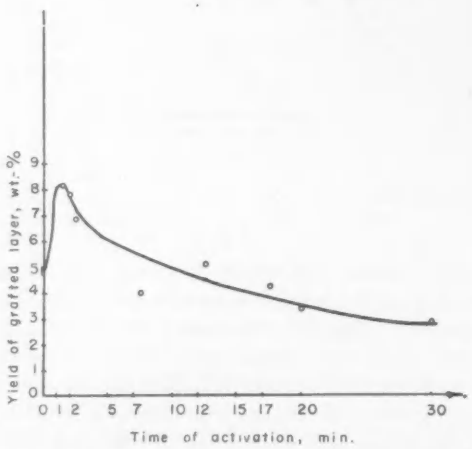


Fig. 10. The effect of the time of thermal treatment of 150°C. on grafting of acrylonitrile to silk.

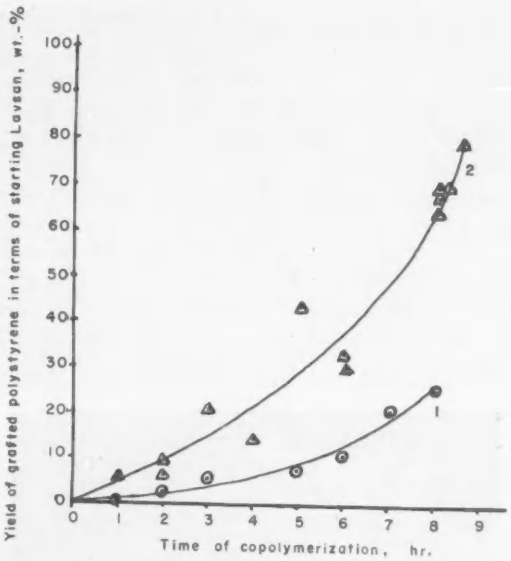


Fig. 11. The dependence of the yield of polystyrene grafted to polyethylene terephthalate on the time of copolymerization at 80°C.: (*1*) samples heated for 30 min. at 100°C.; (*2*) samples heated for 3 min. at 100°C.

ratio of the yield of grafted polystyrene to polyethylene terephthalate depending on the duration of the copolymerization.[11]

In Table I are listed data obtained on grafting acrylonitrile to wool.[12,13]

The study of the reaction of vinyl compounds with different amino acids was undertaken to elucidate the changes undergone by natural fibers under the conditions of graft copolymerization. The experiment showed that the reaction affected most of the cystine, apparently due to the cleavage of the disulfide bond.

TABLE I
Grafting Acrylonitrile to Wool under Various Conditions

No.	Thermal treatment		Addition in weight, %
	Time, min.	Temp., °C.	
1	7.5	100	4.90
2	"	110	5.27
3	"	120	5.15
4	"	130	5.15
5	"	140	5.65
6	"	150	5.15
7	1	170	3.60
8	10	"	3.57

The study of graft copolymers has revealed that the grafting of vinyl monomers to various polymers is of a surface character as seen on the microphotographs in Figures 12 and 13. X-ray investigation has shown that the original structure of the polymer sample was not thereby affected.[8]

The graft polymerization method has proved rather effective in modifying the surface properties of polymers.

The polyethylene terephthalate film becomes adhesive to gelatin after being grafted with a mixture of methyl methacrylate and methacrylic acid.[14,15] Capron fiber, after being grafted to methacrylic acid followed by treatment with copper salt, becomes markedly stable to the degradative effect of elevated temperature.[16,17] Natural fibers (wool and silk) after being grafted with acrylonitrile and methacrylic acid acquire increased stability to fungi.

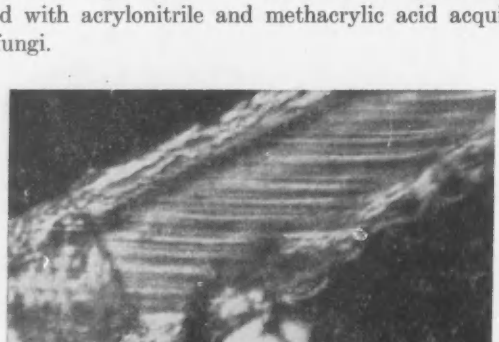
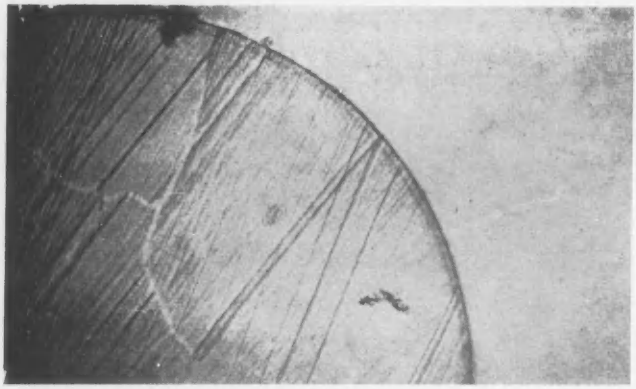


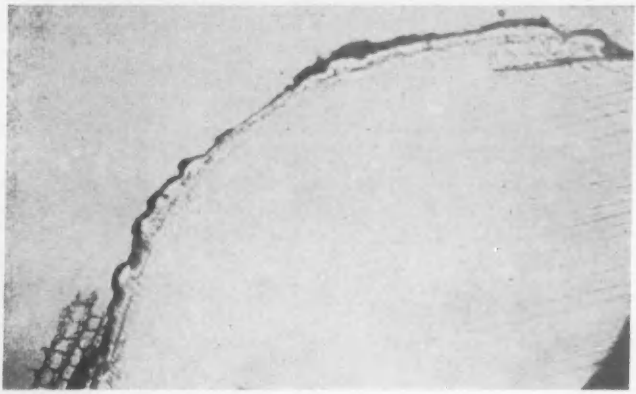
Fig. 12. Cross section of the polyethylene terephthalate film with a grafted layer of polystyrene.

This method of graft copolymerization also proved useful for preparing formerly unknown multicomponent grafted copolymers. This was achieved by first grafting styrene or some other monomer to the polyamide and then, after repeated activation, grafting on another monomer such as methyl methacrylate.

Our investigations have repeatedly shown, that some samples of films and fibers graft vinyl polymers without activation. The grafted layer of vinyl polymer was found to be similar to that grafted to the activated film or fiber sample.[7] We have previously shown that the ability of the polymer to be grafted depends on the time of its exposure to atmospheric conditions as the period of storage is increased. Thus, polyamide or Anide G-669, when freshly prepared, grafts without activation from 2 to 2.5% of polystyrene, whereas a sample stored under the same conditions for several years grafts up to 50%.[7] Evidently, the storage of the particular polymer results in oxidative process that give rise to active centers that initiate graft copolymerization. A similar phenomenon, that is the marked



(*a*)



(*b*)

Fig. 13. Microphotograph of a cross section of Capron monofilament: (*a*) initial monofilament; (*b*) monofilament with a grafted polystyrene layer. ×70.

ability to interact with vinyl monomers without activation was observed with polytrifluorochloroethylene.

We have thus obtained grafted copolymers of polytrifluorochloroethylene with styrene, methyl methacrylate and 2-methyl-5-vinyl-pyridine without using activators. Figure 14 shows the changes in the infrared spectrum of polytrichloroethylene after grafting of styrene and methyl methacrylate. The interaction of vinyl monomers and polytrifluorochloroethylene markedly affects the surface of the film from this polymer and, in particular, increases its adhesion to metals.

On the other hand, it was found that the starting material used to prepare the film, the powdered polytrifluorochloroethylene, practically fails to undergo the reaction of grafted copolymerization. The difference in the reactivity of the powder and the film from polytrifluorochloroethylene may

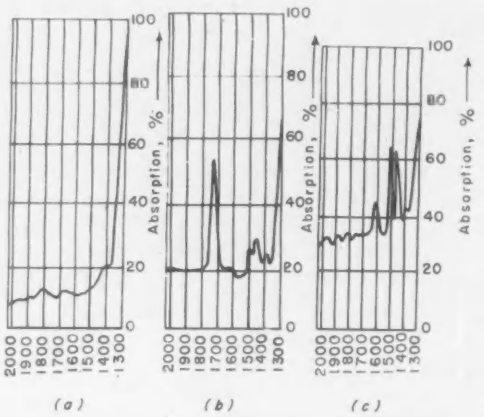


Fig. 14. Change in the infrared spectrum of polytrifluorochloroethylene after grafting of vinyl monomers: (*a*) initial film; (*b*) film with grafted methyl methacrylate; (*c*) film with grafted styrene.

be accounted for by the changes in the chemical composition and the structure of the polymer resulting from processing the powder to a film.

According to the literature, heating polytrifluorochloroethylene up to 300°C. leads to thermoxidative destruction of the polymer. It is accompanied by the formation of unsaturated —C=C— bonds of anhydrides and acids.[18,19]

When unsaturated, polymers may give rise to unstable peroxide products:

$$R_F—CF=CF_2 \rightarrow R—\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{CF}}—CF_2$$

(where R_F is a fluorocarbon radical) that can initiate the subsequent graft copolymerization.[20] The analysis of the liquid degradation product of the powdered polytrifluorochloroethylene has indeed shown it to contain 0.07–0.08% of activated oxygen. This led us to suggest that the processing of the powdered polytrifluorochloroethylene to a film should always be accompanied by some degradation of the polymer leading thereby to a small amount of unsaturation. Careful examination of infrared spectra of the film under investigation has revealed weak absorption bands not previously observed in the absorption spectrum of the powder in the absorption region of the groups[21] $R_F—CF=CF_2$ (5.60 μ), $(R_F)_2C=CF_2$ (5.73–5.79 μ), $R_F—CF=CF—R_F$ (5.78 μ), and R_FCOOH (5.54–5.65 μ), R_F being either $Cl(CF_2—CFCl)_3CF_2$, or a polymer. We have additionally heated such a film in the air at 300°C. for 5 hr. This led to increased intensity of the absorption band at 5.55–5.60 μ and to the appearance of a new band at 5.31 μ. These bands can be assigned to the absorption of the groups[19,21] $R_F—CF=CF_2$ and RF—C(F)=O.

We have similarly noted the effect of the mode of film processing on the activity of the film from other polymers, for instance, with polyethylene terephthalate and Capron. This led us to the conclusion that the grafting of vinyl monomers to polymers is an extremely sensitive indicator of the availability of active centers that are capable of reacting with vinyl monomers.

The process of graft copolymerization is also affected by many other factors, such as the surface condition of the polymer, the proportion of crystalline and amorphous regions, and the orientation of films and fibers.

In summary, surface grafting is a rather effective method that makes possible an extensive modification of the surface properties of products from various polymers.

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Synopsis

Obtaining graft copolymers on the surface of films, fibers, and other fabrics is an effective method of controlling the properties of the polymer surface. In the present work products from various polymer materials have been studied: films and fibers from polyamides, polyesters, films from fluorinated plastics, and natural fibers (wool and silk). Vinyl compounds used included styrene, methyl methacrylate, methyl-acrylate, acrylonitrile, acrylic and methacrylic acids, and 2-methyl-5-vinyl-pyridine. As activating agents ozone and air oxygen were used. The treatment of the polymers with ozone and oxygen leads to the formation of different oxidation products in them including peroxide compounds whose decomposition later initiates the graft copolymerization. The study of the graft copolymers obtained has showed that they combine the properties of the two polymers and allow the properties to be varied to a large extent.

Résumé

La formation de copolymères greffés sur la surface de films de fibres et d'autres tissus est une méthode efficace pour contrôler les propriétés de ces surfaces polymériques. Dans ce travail on a étudié des substances provenant de différents matériaux polymériques: des films et des fibres de polyamides, des polyesters, des films de plastiques fluorés, et des fibres naturelles (de la laine et de la soie). Comme composés vinyliques on emploie: le styrène, le méthacrylate de méthyle, l'acrylate de méthyle, l'acrylonitrile, les acides méthacrylique et acrylique, la 2-methyl-5-vinyl-pyridine et d'autres. L'ozone et l'oxygène de l'air servent comme agents d'activation. Le traitement de ces polymères avec l'ozone et l'oxygène conduit à la formation de différents produits d'oxydation, y compris des composés peroxydés, dont la décomposition initie plus tard la copolymérisation greffés. L'étude des copolymères greffés obtenus, montre qu'ils possèdent les propriétés des deux polymères, et permettent de les modifier dans une large mesure.

Zusammenfassung

Die Bildung von Pfropfcopolymeren an der Oberfläche von Filmen, Fasern und anderen Stoffen eine wirksame Methode zur Modifizierung von Polymeroberflächen dar. In der vorliegenden Arbeit wurden Proben von verschiedenen Materialien untersucht: Polyamidfilme und -fasern, Filme aus fluorierten Kunststoffen und natürliche Fasern (Wolle und Seide). Als Vinylverbindungen wurden Styrol, Methylmethacrylat, Methylacrylat, Acrylnitril, Acryl- und Methacylsäure, 2 Methyl-5-vinylpyridin u.a. verwendet. Als aktivierendes Agens fanden Ozon und Luftsauerstoff Verwendung. Die Behandlung der Polymeren mit Ozone und Sauerstoff führte Bildung verschiedener Oxydationsprodukte einschliesslich Peroxydverbindungen, deren Zersetzung später die Pfropfcopolymerisation startet. Die Untersuchung der hergestellten Pfropfcopolymeren ergab, dass diese die Eigenschaften beider Polymeren in sich vereinigen und eine weitgehende Veränderung derselben erlauben.

Discussion

Y. Landler (*Kléber-Colombes, Paris, France*): Le Professeur Korshak et ses collaborateurs ont trouvé qu'au cours de l'ozonisation des polyamides on arrive à une valeur limite en oxygène actif et qu'on observe en même temps une dégradation du polymère. Les travaux faits dans notre laboratorie depuis une dizaine d'années sur le greffage par l'ozone des différents polymères ont montré un comportement particulier des polyamides. En effet l'humidité que ce polymère peut contenir provoque, même à la température ambiante, la décomposition des groupements peroxydiques formés sous l'action de l'ozone. De ce fait la valeur limite de l'oxygène active observée est liée à la teneur en humidité des polyamides. Si des précautions suffisantes sont prises, on peut augmenter la teneur en oxygène actif suivant une loi linéaire avec la dose d'ozone et dans ce cas aucune dégradation perceptible n'est observée.